BOOKS IN SOILS, PLANTS, AND THE ENVIRONMENT

Editorial Board

Agricultural Engineering
Robert M Peart, University of Florida, Gainesville

Animal Science
Harold Hafs, Rutgers University, New Brunswick, New Jersey

Crops
Mohammad Pessarakhi, University of Arizona, Tucson

Irrigation and Hydrology
Donald R Nielsen, University of California, Davis

Microbiology
Jan Dirk van Elsas, Research Institute for Plant Protection, Wageningen, The Netherlands

Plants
L David Kuykendall, U S Department of Agriculture, Beltsville, Maryland

Soils
Jean-Marc Bollag, Pennsylvania State University, University Park, Pennsylvania
Tsuyoshi Miyazaki, University of Tokyo

Soil Biochemistry, Volume 1, edited by A D McLaren and G H Peterson
Soil Biochemistry, Volume 2, edited by A D McLaren and J Skujinis
Soil Biochemistry, Volume 3, edited by E A Paul and A D McLaren
Soil Biochemistry, Volume 4, edited by E A Paul and A D McLaren
Soil Biochemistry, Volume 5, edited by E A Paul and J N Ladd
Soil Biochemistry, Volume 6, edited by Jean-Marc Bollag and G Stotzky
Soil Biochemistry, Volume 7, edited by G Stotzky and Jean-Marc Bollag
Soil Biochemistry, Volume 8, edited by Jean-Marc Bollag and G Stotzky
Soil Biochemistry, Volume 9, edited by G Stotzky and Jean-Marc Bollag
Soil Biochemistry, Volume 10, edited by Jean-Marc Bollag and G Stotzky

Organic Chemicals in the Soil Environment, Volumes 1 and 2, edited by C A I Goring and J W Hamaker

Humic Substances in the Environment, M Schnitzer and S U Khan

Microbial Life in the Soil An Introduction, T Hatton

Principles of Soil Chemistry, Kim H Tan

Soil Analysis Instrumental Techniques and Related Procedures, edited by Keith A Smith

Soil Reclamation Processes Microbiological Analyses and Applications, edited by Robert L Tate III and Donald A Klein

Symbiotic Nitrogen Fixation Technology, edited by Gerald H Elkan

Soil–Water Interactions Mechanisms and Applications, Shingo Iwata and Toshio Tabuchi with Benno P Warkentin
Soil Analysis: Physical Methods, edited by Keith A. Smith and Chris E. Mullins
Growth and Mineral Nutrition of Field Crops, N. K. Fageria, V. C. Baligar, and Charles Allan Jones
Semiarid Lands and Deserts: Soil Resource and Reclamation, edited by J. Skujins
Plant Roots: The Hidden Half, edited by Yoav Waisel, Amram Eshel, and Uzi Kafkafi
Plant Biochemical Regulators, edited by Harold W. Gausman
Maximizing Crop Yields, N. K. Fageria
Transgenic Plants: Fundamentals and Applications, edited by Andrew Hiatt
Water Flow in Soils, edited by Tsuyoshi Miyazaki
Handbook of Plant and Crop Stress, edited by Mohammad Pessarakli
Genetic Improvement of Field Crops, edited by Gustavo A. Slafer
Agricultural Field Experiments: Design and Analysis, Roger G. Petersen
Environmental Soil Science, Kim H. Tan
Mechanisms of Plant Growth and Improved Productivity: Modern Approaches, edited by Amarjit S. Basra
Selenium in the Environment, edited by W. T. Frankenberger, Jr., and Sally Benson
Plant–Environment Interactions, edited by Robert E. Wilkinson
Handbook of Plant and Crop Physiology, edited by Mohammad Pessarakli
Handbook of Phytoalexin Metabolism and Action, edited by M. Daniel and R. P. Purkayastha
Stored-Grain Ecosystems, edited by Digvir S. Jayas, Noel D. G. White, and William E. Muir
Agrochemicals from Natural Products, edited by C. R. A. Godfrey
Seed Development and Germination, edited by Jaime Kigel and Gad Galli
Nitrogen Fertilization in the Environment, edited by Peter Edward Bacon
Phytohormones in Soils: Microbial Production and Function, William T. Frankenberger, Jr., and Muhammad Arshad
Handbook of Weed Management Systems, edited by Albert E. Smith
Soil Sampling, Preparation, and Analysis, Kim H. Tan
Soil Erosion, Conservation, and Rehabilitation, edited by Menachem Agassi
Photoassimilate Distribution in Plants and Crops: Source–Sink Relationships, edited by Eli Zamski and Arthur A. Schaffer
Mass Spectrometry of Soils, edited by Thomas W. Boutton and Shinichi Yamasaki
Handbook of Photosynthesis, edited by Mohammad Pessarakli
Soil and Plant Analysis in Sustainable Agriculture and Environment, edited by Teresa Hood and J. Benton Jones, Jr.
Modern Soil Microbiology, edited by J. D. van Elsas, J. T. Trevors, and E. M. H. Wellington
Fungal Pathogenesis in Plants and Crops: Molecular Biology and Host Defense Mechanisms, P. Vidhyasekaran
Plant Pathogen Detection and Disease Diagnosis, P. Narayanasamy
Agricultural Systems Modeling and Simulation, edited by Robert M. Peart and R. Bruce Curry
Agricultural Biotechnology, edited by Arie Altman
Plant–Microbe Interactions and Biological Control, edited by Greg J. Boland and L. David Kuykendall
Environmental Chemistry of Selenium, edited by William T. Frankenberger, Jr., and Richard A. Engberg
Sulfur in the Environment, edited by Douglas G. Maynard
Soil–Machine Interactions: A Finite Element Perspective, edited by Jie Shen and Radhey Lal Kushwaha
Mycotoxins in Agriculture and Food Safety, edited by Kaushal K. Sinha and Deepak Bhatnagar
Plant Amino Acids: Biochemistry and Biotechnology, edited by Bijay K. Singh
Handbook of Functional Plant Ecology, edited by Francisco I. Pugnaire and Fernando Valladares
Plant Responses to Environmental Stresses: From Phytohormones to Genome Reorganization, edited by H. R. Lerner
Handbook of Pest Management, edited by John R. Ruberson
Microbial Endophytes, edited by Charles W. Bacon and James F. White, Jr.
Microbial Pest Control, Sushil K. Khetan
The Rhizosphere: Biochemistry and Organic Substances at the Soil–Plant Interface, Roberto Pinton, Zeno Varanini, and Paolo Nannipieri
Woody Plants and Woody Plant Management: Ecology, Safety, and Environmental Impact, Rodney W. Bovey
Metals in the Environment: Analysis by Biodiversity, M. N. V. Prasad
Plant Pathogen Detection and Disease Diagnosis: Second Edition, Revised and Expanded, P. Narayanasamy
Environmental Chemistry of Arsenic, edited by William T. Frankenberger, Jr.
Handbook of Plant Growth: pH as the Master Variable, edited by Zdenko Rengel
Biological Control of Crop Diseases, edited by Samuel S. Gnanamanickam
Pesticides in Agriculture and the Environment, edited by Willis B. Wheeler
Mathematical Models of Crop Growth and Yield, Allen R. Overman and Richard V. Scholtz III
Plant Biotechnology and Transgenic Plants, edited by Kirsi-Marja Oksman-Caldentey and Wolfgang H. Barz
Handbook of Soil Acidity, edited by Zdenko Rengel

Additional Volumes in Preparation

Humic Matter: Issues and Controversies in Soil and Environmental Science, Kim H. Tan
Molecular Host Resistance to Pests, S. Sadasivam and B. Thayumanavan
Soil acidity is one of the most prevalent problems in production of food and fiber because at least 40%, and by some estimates as much as 70%, of the world’s arable land is affected. With increased pressure to produce more food for the expanding population of this planet and with urbanization claiming large chunks of arable land, agriculture is pushed more and more into marginal land plagued with edaphic and other stresses, including acidity.

Soils become acidic during geological evolution, especially in areas of high rainfall, because bases are relatively easy to leach from soils, leaving them acidic. In addition, soil acidification is frequently inevitable in agriculture that relies on either N₂ fixation or cheaper (ammonium-containing) N fertilizers and on export of organic material from paddocks, thus disturbing N and C cycles. In some parts of the world, acidification due to deposition of acidic rain is also important.

Although liming can effectively increase soil pH and thus ameliorate acidic soils, the large amounts required and the absence of lime pits positioned close to the paddocks where lime is needed make soil liming an expensive option in many situations. In addition, liming subsoil is technically difficult and may be economically unprofitable in many soils. Therefore, other management options need to be employed either in isolation or together with liming to allow continuity of food and fiber production on land with a high acidification potential.

There are four subject areas in this book: (1) soil acidification (global distribution of acidic and acidifying soils, mechanisms governing the acidification, modeling acidification in space and time, producing maps of soil acidification risk), (2) measurement of acidity (including spatial and temporal variability on the micro- and macroscale), (3) growth-inhibiting factors associated with acids soils (e.g., ion toxicity, nutrient deficiency), and (4) management of acidification and acidity in agriculture and forestry, including aspects of chemical amelioration of soils, growing resistant plants, and adapted farming systems, and finishing with the role of pH in phytoremediation of metal-contaminated soils. Therefore, in
comprehensively characterizing the role of soil acidity and its amelioration in soil fertility, health, and productivity, the book covers a wide range of topics that genuinely span such scientific disciplines as agronomy, forestry, soil science, plant biology, breeding, ecology, modeling, land rehabilitation, and conservation.

All chapters have been reviewed according to the standard of high-impact international journals. I would like to thank the contributors, who patiently went through a number of revisions of their chapters. I would also like to thank the Marcel Dekker, Inc., staff for capable handling of numerous issues and for their dedication to producing a high-quality multidisciplinary book.

Zdenko (Zed) Rengel
Contents

Preface iii
Contributors vii

1. Soil Acidification: The World Story 1
   Malcolm E. Sumner and Andrew D. Noble

2. Role of Carbon, Nitrogen, and Sulfur Cycles in Soil Acidification 29
   Nanthi S. Bolan and Mike J. Hedley

3. Role of Plant Cation/Anion Uptake Ratio in Soil Acidification 57
   Caixan Tang and Zdenko Rengel

4. Acid Inputs into the Soils from Acid Rain 83
   Christine Alewell

5. Quantifying the Acid Balance for Broad-Acre Agricultural Systems 117
   James Fisher, Art Diggle, and Bill Bowden

6. Modeling Acidification Processes in Agricultural Systems 135

7. Using Geographic Information Systems (GISs) in Soil Acidification Risk Assessments 189
   Patricia A. Hill

8. Micro- and Macroscale Heterogeneity of Soil Acidity 209
   Bernhard Manderscheid
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Author(s)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Measurements of H⁺ Fluxes and Concentrations in the Rhizosphere</td>
<td>Benoît Jaillard, Claude Plassard, and Philippe Hinsinger</td>
<td>231</td>
</tr>
<tr>
<td>10</td>
<td>Toxic Elements in Acid Soils: Chemistry and Measurement</td>
<td>Neal W. Menzies</td>
<td>267</td>
</tr>
<tr>
<td>11</td>
<td>Using Lime to Ameliorate Topsoil and Subsoil Acidity</td>
<td>Doug C. Edmeades and Anna M. Ridley</td>
<td>297</td>
</tr>
<tr>
<td>12</td>
<td>Role of Organic Matter in Alleviating Soil Acidity</td>
<td>M. T. F. Wong and R. S. Swift</td>
<td>337</td>
</tr>
<tr>
<td>13</td>
<td>Fertility Management of Tropical Acid Soil for Sustainable Crop Production</td>
<td>Nand K. Fageria and Virupax C. Baligar</td>
<td>359</td>
</tr>
<tr>
<td>14</td>
<td>Role of the Genotype in Tolerance to Acidity and Aluminum Toxicity</td>
<td>David F. Garvin and Brett F. Carver</td>
<td>387</td>
</tr>
<tr>
<td>15</td>
<td>Managing Soil Acidification Through Crop Rotations in Southern Australia</td>
<td>David R. Coventry, Alireza Farhoodi, and Ren-kou K. Xu</td>
<td>407</td>
</tr>
<tr>
<td>16</td>
<td>Managing Acidification and Acidity in Forest Soils</td>
<td>Douglas L. Godbold</td>
<td>431</td>
</tr>
<tr>
<td>17</td>
<td>Role of pH in Phytoremediation of Contaminated Soils</td>
<td>Jianwei W. Huang and Jianjun Chen</td>
<td>449</td>
</tr>
</tbody>
</table>

Index 473
Contributors

Christine Alewell  Department of Soil Ecology, BITÖK, University of Bayreuth, Bayreuth, Germany

Virupax C. Baligar  Alternate Crops and Systems Laboratory, Beltsville Agricultural Research Center, USDA-ARS, Beltsville, Maryland, U.S.A.

Nanthi S. Bolan  Soil and Earth Sciences Group, Massey University, Palmerston North, New Zealand

Bill Bowden  The University of Western Australia, Perth, and Centre for Cropping Systems, Department of Agriculture Western Australia, Northam, Australia

Jörg Braschkat  CSIRO Plant Industry, Canberra, Australia

Brett F. Carver  Department of Plant and Soil Sciences, Oklahoma State University, Stillwater, Oklahoma, U.S.A.

Jianjun Chen  Mid-Florida Research and Education Center, University of Florida, Apopka, Florida, U.S.A.

David R. Coventry  Department of Agronomy and Farming Systems, Adelaide University, Roseworthy Campus, Adelaide, Australia

Art Diggle  The University of Western Australia, Perth, and Department of Agriculture Western Australia, Bentley, Australia

Doug C. Edmeades  agKnowledge Ltd., Hamilton, New Zealand

Nand K. Fageria  National Rice and Bean Research Center of EMBRAPA, Santo Antônio de Goiás, Brazil

Alireza Farhoodi  Department of Agronomy and Farming Systems, Adelaide University, Roseworthy Campus, Adelaide, Australia
James Fisher  The University of Western Australia, Perth, and Centre for Cropping Systems, Department of Agriculture Western Australia, Northam, Australia

David F. Garvin  Plant Science Research Unit, USDA-ARS, St. Paul, Minnesota, U.S.A.

Douglas L. Godbold  School of Agricultural and Forest Sciences, University of Wales, Bangor, Gwynedd, United Kingdom

John N. G. Hargreaves  CSIRO Sustainable Ecosystems and APSRU, Toowoomba, Australia

Mike J. Hedley  Soil and Earth Sciences Group, Massey University, Palmerston North, New Zealand

Keith R. Helyar  Agricultural Research Institute, NSW Agriculture, Wagga Wagga, Australia

Patricia A. Hill  Department of Agriculture Western Australia, Ravensthorpe, Australia

Philippe Hinsinger  UMR Soil and Environment, INRA, Montpellier, France

Zvi Hochman  CSIRO Sustainable Ecosystems and APSRU, Toowoomba, Australia

Jianwei W. Huang  Lockheed Martin/REAC, Edison, New Jersey, U.S.A.

Benoît Jaillard  UMR Soil and Environment, INRA, Montpellier, France

Bernhard Manderscheid  Forest Research Station, Göttingen, Germany

Neal W. Menzies  School of Land and Food Sciences, The University of Queensland, St. Lucia, Australia

Andrew D. Moore  CSIRO Plant Industry, Canberra, Australia

Andrew D. Noble  Land and Water, CSIRO, Townsville, Australia

Claude Plassard  UMR Soil and Environment, INRA, Montpellier, France

Mervyn E. Probert  CSIRO Sustainable Ecosystems and APSRU, Indooroopilly, Queensland, Australia

Zdenko Rengel  Department of Soil Science and Plant Nutrition, The University of Western Australia, Perth, Australia

Anna M. Ridley  Agriculture Victoria, Rutherglen, Australia

Richard J. Simpson  CSIRO Plant Industry, Canberra, Australia
Contributors

Malcolm E. Sumner  Department of Crop and Soil Sciences, University of Georgia, Athens, Georgia, U.S.A.

R. S. Swift  Faculty of Natural Resources, Agriculture and Veterinary Science, The University of Queensland, Brisbane, Australia

Caixan Tang  Department of Soil Science and Plant Nutrition, The University of Western Australia, Perth, Australia

Kirsten Verburg  CSIRO Land and Water and APSRU, Canberra, Australia

M. T. F. Wong  CSIRO Land and Water, Wembley, and The University of Western Australia, Perth, Australia

Ren-kou Xu  Department of Soil Electrochemistry, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, P.R. China
Soil Acidification: The World Story

Malcolm E. Sumner  
University of Georgia, Athens, Georgia, U.S.A.  

Andrew D. Noble  
Land and Water, CSIRO, Townsville, Australia

1 INTRODUCTION

For decades, soil acidity has been a major constraint to crop production throughout the world. However, in developed nations, the use of lime to counteract acidity in high-input agriculture over the past 50 to 100 years has led to a marked decrease in the area of acid soils under cultivation and to spectacular increases in yields. Still, in the case of deep naturally acid profiles, little amelioration of subsoil acidity has occurred, and in some cases (e.g., in Australia), neutral to alkaline subsoils have actually been acidified as a result of the failure to correct topsoil acidity [1]. In contrast, in developing nations with largely low-input agriculture and farmers able to afford only minimal applications of lime, very little amelioration of soil acidity has taken place. In fact, the condition has probably worsened in many areas.

Experimental results [2] show that counteracting subsoil acidity can result in substantial (20–100%) yield responses, particularly under rain-fed conditions. There are a number of reasons for this situation. Many soils in developing nations are naturally very acid and infertile to great depths in the profile. Cultivation of such soils without inputs results in very low yields, which has maintained the farming population in poverty. As a result, farming has mined what little resources
the soils have had to offer and yields have tended to decrease rather than increase with time for lack of adequate inputs.

Without access to financial loans to facilitate the purchase of inputs, it is extremely difficult for these resource-poor farmers to break out of this cycle of poverty. The small loans required by such farmers are seldom available from traditional lending institutions. Despite the results of several years of research which have shown that yields can be more than doubled by the application of lime to acid soils, this practice has not been widely adopted in developing nations because of the unavailability or high cost of lime, the lack of access to loans, and poor infrastructure capacity.

Poor crop growth on acid soils is usually a direct result of aluminum toxicity. When soil pH$_{H2O}$ drops below 5, aluminum becomes soluble and causes severe root pruning that results in reduced water and nutrient uptake (see Chapter 10). Thus, one of the first manifestations of the harmful effects of soil acidity is drought stress. Many of the acid soils in developing nations are deep and well drained and have high yield potentials if the roots could penetrate and extract water from the acid subsoils, normally beyond their reach [3]. The limiting factors associated with poor root penetration are the lack of Ca$_{2}^{+}$ and/or excess Al$_{3}^{3+}$. The efficient use of subsoil water again requires inputs such as gypsum and lime, which have been shown to promote yields on soils with acid highly weathered subsoils throughout the world [4]. A simple test is available to identify subsoils likely to respond to gypsum [3]. Thus, the solution to the problem of soil acidity in developing nations does not require more research but rather an aggressive extension program to promote the use of lime, gypsum, and other inputs (phosphorus, nitrogen, potassium, etc.) whose benefits have been amply demonstrated. This should be coupled with an appropriate system for making small production loans to farmers [5]. It is often not appreciated that soil acidification is a severe degradation process. Consequently, its remediation should be seen as a capital cost, which can be amortized over a number of years.

2 AREAL EXTENT OF ACID SOILS

Estimates of the total area of topsoils affected by acidity throughout the world vary from $3.777 \times 10^9$ [6] to $3.950 \times 10^9$ [7] ha, representing approximately 30% of the total ice-free land area of the world. The distribution of acid soils by region in relation to cultivated and total ice-free land area is presented in Table 1. The largest areas of acid soils are in South America, North America, Asia, and Africa. In most regions, the area of acid soils far exceeds the area under cultivation, indicating that large areas of acid soils are still under natural forest or grassland vegetation. The total area affected by subsoil acidity is estimated as $2.918 \times 10^9$ ha [6], meaning that approximately 75% of the acid soils of the world suffer from subsoil limitations due to acidity.
<table>
<thead>
<tr>
<th>Class</th>
<th>World</th>
<th>Africa</th>
<th>Australia/New Zealand</th>
<th>Europe</th>
<th>Near East</th>
<th>Far East</th>
<th>Southeast and Pacific</th>
<th>North Central</th>
<th>North</th>
<th>Central</th>
<th>South</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid land ($\times 10^9$ ha)</td>
<td>3.950</td>
<td>0.659</td>
<td>0.239</td>
<td>0.391</td>
<td>0.005</td>
<td>0.212</td>
<td>0.314</td>
<td>0.512</td>
<td>0.662</td>
<td>0.036</td>
<td>0.916</td>
</tr>
<tr>
<td>Total land ($\times 10^9$ ha)</td>
<td>13.15</td>
<td>3.01</td>
<td>0.82</td>
<td>0.48</td>
<td>0.50</td>
<td>1.48</td>
<td>0.40</td>
<td>0.85</td>
<td>2.11</td>
<td>0.10</td>
<td>1.75</td>
</tr>
<tr>
<td>Acid/total (%)</td>
<td>30</td>
<td>22</td>
<td>30</td>
<td>37</td>
<td>1</td>
<td>12</td>
<td>63</td>
<td>57</td>
<td>30</td>
<td>35</td>
<td>52</td>
</tr>
<tr>
<td>Cultivated land ($\times 10^9$ ha)</td>
<td>1.4</td>
<td>0.158</td>
<td>0.032</td>
<td>0.154</td>
<td>0.519</td>
<td>0.239</td>
<td>0.077</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cultivated/total (%)</td>
<td>10.6</td>
<td>5.2</td>
<td>3.9</td>
<td>32.1</td>
<td>18.9</td>
<td>11.3</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Source: Data from Ref. 7.*
Using a scale for acid intensity based on pH ranges of <3.5 (extreme), 3.5–4.5 (high), 4.5–5.5 (moderate), and 5.5–6.5 (slight), the global distribution of these acid topsoils and subsoils is depicted in Figs. 1 and 2. Areas associated with each of these subdivisions are tabulated by region in Table 2. On a global basis, only a relatively small proportion of acid topsoils fall in the extremely acid category, with South America accounting for the lion’s share. The remaining acid soils are fairly evenly distributed among the other categories. Except for the extremely acid category, a similar pattern is exhibited for subsoils. In the Americas, Africa, and Asia, a large proportion of soils with topsoil acidity also exhibit marked subsoil acidity of similar intensity, indicating the strong linkage between top- and subsoil acidity under pristine conditions. Because $\text{Al}^{3+}$ becomes soluble and toxic below pH $\sim$ 5.0 to 5.2, the categories of moderate and high acidity are of particular interest in agronomic terms, accounting for 67 and 79% of the world’s acid topsoils and subsoils, respectively.

In Tables 3 and 4, the areal extent of acid topsoils has been broken down according to the Food and Agriculture Organization (FAO) Soil Groups [8] and Soil Taxonomy [9] Orders. As one would expect, the largest areas of acid soils occur in Soil Groups that have been either intensely weathered [Acrisols, Nitosols, Ferralsols] (Ultisols, Oxisols) or formed on basic cation-poor parent materials [Podzols, Histosols, Arenosols, Podzoluvisols, Cambisols] (Entisols, Spodosols, Inceptisols, Histosols).

The preceding estimates (Tables 1–4) should be treated with some caution as they are derived from databases that contain significant omissions, possibly inappropriate extrapolations and assumptions, and unspecified methods of measuring pH and have not been georeferenced [6]. However, they are the best estimates available at present.

3 TYPES OF ACID SOILS

3.1 Naturally Occurring Acid Soils

3.1.1 Due to Intensive Weathering

The natural weathering processes for acid soils involve leaching of the parent material by acidic rain due to the presence of $\text{H}_2\text{CO}_3$ that provides protons and removes basic cations in the leachate. As a result, parent rocks weather to form acid soils with the rate of acidification depending on the nature of the parent material, effective rainfall, and temperature. Highly basic parent materials weather more rapidly than highly siliceous substrates, with both increased rainfall and temperature promoting the process. Under extreme conditions such as occur in the humid tropics, most silicate minerals in the parent material are weathered away by desilication, leaving little other than the oxides of iron and aluminum. Such soils (Oxisols and Ultisols) are usually weathered to great depths. Thus, in nature, one finds
FIGURE 1  Global distribution of soils with acid topsoils. (Reprinted with permission. Copyright Courtesy Natural Resource Conservation Service, USDA, USA.)
Figure 2. Global distribution of soils with acid subsoils. (Reprinted with permission. Courtesy Natural Resource Conservation Service, USDA, USA.)
<table>
<thead>
<tr>
<th>Class</th>
<th>America</th>
<th></th>
<th></th>
<th></th>
<th>Europe</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>World Top</td>
<td>Sub</td>
<td></td>
<td></td>
<td></td>
<td>South and East Asia</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slight (pH_{H_2O} 5.5–6.5)</td>
<td>1.25</td>
<td>0.58</td>
<td>0.21</td>
<td>0.11</td>
<td>0.25</td>
<td>0.12</td>
<td>0.43</td>
</tr>
<tr>
<td>Moderate (pH_{H_2O} 4.5–5.5)</td>
<td>1.54</td>
<td>1.38</td>
<td>0.30</td>
<td>0.28</td>
<td>0.44</td>
<td>0.42</td>
<td>0.33</td>
</tr>
<tr>
<td>High (pH_{H_2O} 3.5–4.5)</td>
<td>0.98</td>
<td>0.95</td>
<td>0.09</td>
<td>0.09</td>
<td>0.36</td>
<td>0.36</td>
<td>0.12</td>
</tr>
<tr>
<td>Extremely acid (pH_{H_2O} &lt; 3.5)</td>
<td>0.15</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.13</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>3.78</td>
<td>2.92</td>
<td>0.60</td>
<td>0.49</td>
<td>1.18</td>
<td>0.90</td>
<td>0.88</td>
</tr>
</tbody>
</table>

*Source:* Data from Ref. 6.
**Table 3** Areal Extent (× 10^6 ha) of Acid Topsoils for the FAO Soil Groups

<table>
<thead>
<tr>
<th>Soil Group</th>
<th>World</th>
<th>Africa</th>
<th>Australia and New Zealand</th>
<th>Near East</th>
<th>Europe</th>
<th>Asia</th>
<th>Southeast and Pacific</th>
<th>North and Central</th>
<th>America</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluvisols</td>
<td>50</td>
<td>13</td>
<td>0</td>
<td>NA</td>
<td>1</td>
<td>5</td>
<td>19</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Gleysols</td>
<td>402</td>
<td>57</td>
<td>1</td>
<td>NA</td>
<td>27</td>
<td>6</td>
<td>19</td>
<td>136</td>
<td>84</td>
</tr>
<tr>
<td>Regosols</td>
<td>293</td>
<td>26</td>
<td>97</td>
<td>NA</td>
<td>6</td>
<td>5</td>
<td>1</td>
<td>52</td>
<td>93</td>
</tr>
<tr>
<td>Arenosols</td>
<td>280</td>
<td>101</td>
<td>83</td>
<td>2</td>
<td>NA</td>
<td>0</td>
<td>5</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Rankers</td>
<td>61</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>18</td>
<td>26</td>
<td>4</td>
<td>1</td>
<td>NA</td>
</tr>
<tr>
<td>Andosols</td>
<td>34</td>
<td>1</td>
<td>2</td>
<td>NA</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Cambisols</td>
<td>300</td>
<td>26</td>
<td>12</td>
<td>0</td>
<td>59</td>
<td>21</td>
<td>45</td>
<td>28</td>
<td>66</td>
</tr>
<tr>
<td>Podzoluvicos</td>
<td>255</td>
<td>NA</td>
<td>NA</td>
<td>75</td>
<td>8</td>
<td>0</td>
<td>168</td>
<td>4</td>
<td>NA</td>
</tr>
<tr>
<td>Podzols</td>
<td>415</td>
<td>11</td>
<td>11</td>
<td>NA</td>
<td>146</td>
<td>1</td>
<td>4</td>
<td>23</td>
<td>209</td>
</tr>
<tr>
<td>Planosols</td>
<td>15</td>
<td>0</td>
<td>8</td>
<td>NA</td>
<td>2</td>
<td>NA</td>
<td>1</td>
<td>NA</td>
<td>2</td>
</tr>
<tr>
<td>Acrisols</td>
<td>731</td>
<td>86</td>
<td>12</td>
<td>0</td>
<td>3</td>
<td>126</td>
<td>164</td>
<td>NA</td>
<td>94</td>
</tr>
<tr>
<td>Nitossols</td>
<td>118</td>
<td>60</td>
<td>2</td>
<td>NA</td>
<td>7</td>
<td>16</td>
<td>NA</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Ferralsols</td>
<td>727</td>
<td>278</td>
<td>9</td>
<td>NA</td>
<td>0</td>
<td>0</td>
<td>16</td>
<td>NA</td>
<td>0</td>
</tr>
<tr>
<td>Histosols</td>
<td>270</td>
<td>NA</td>
<td>1</td>
<td>NA</td>
<td>54</td>
<td>8</td>
<td>17</td>
<td>97</td>
<td>91</td>
</tr>
<tr>
<td>Total</td>
<td>3950</td>
<td>659</td>
<td>239</td>
<td>5</td>
<td>391</td>
<td>212</td>
<td>315</td>
<td>512</td>
<td>662</td>
</tr>
</tbody>
</table>

*Source:* Data from Ref. 7.
a range of soils in different stages of weathering exhibiting different degrees of acidity often reflected in the systems used to classify soils.

In terms of soil taxonomy [9], acid soils in this category fall mainly into four Soil Orders, namely Oxisols (Ferralsols), Ultisols (Acrisols, Nitosols, Planosols), Andisols (Andosols), and Alfisols (Podzoluvisols). The nearest FAO Soil Group equivalents have been placed in parentheses. Some highly acid soils (acid sulfate) also occur in the Inceptisol Order.

Oxisols are the most highly weathered but not necessarily the most acidic soils (Table 5) because, in the final stages of weathering, soil pH increases due to the high point of zero charge ($\text{pH}_\text{ZPC}$) of Fe and Al oxides. They have very low basic cation status and effective cation exchange capacity (ECEC), but exhibit appreciable variable charge indicated by the difference [cation exchange capacity (CEC) − ECEC]. In this context, CEC refers to the value obtained with 1 M $\text{NH}_4\text{OAc (pH 7)}$, and ECEC is the sum of exchangeable cations ($\text{Al}^{3+} + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^{+} + \text{Na}^{+}$). Often they are heavy textured with a more or less uniform distribution of clay with depth. They are extremely poor in available phosphorus but usually have adequate to excellent physical properties.

Ultisols are less highly weathered but often more acid than Oxisols and usually contain appreciable amounts of silicate clay minerals (mainly kaolinite). Clay content increases with depth often abruptly, giving rise to a Bt horizon. In general, their ECEC values are higher than for Oxisols but they also exhibit considerable variable charge. They contain appreciable levels of toxic exchangeable aluminum to depth associated with low basic cation status (Table 5). Unfortunately, the NRCS-USDA database [13] does not contain information on exchangeable $\text{Al}^{3+}$ and, consequently, many values are missing in Table 5.

<table>
<thead>
<tr>
<th>Order</th>
<th>Area ($\times 10^9$ ha)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entisols</td>
<td>0.824</td>
<td>20.9</td>
</tr>
<tr>
<td>Inceptisols</td>
<td>0.561</td>
<td>14.2</td>
</tr>
<tr>
<td>Andisols</td>
<td>0.034</td>
<td>0.9</td>
</tr>
<tr>
<td>Spodosols</td>
<td>0.415</td>
<td>10.5</td>
</tr>
<tr>
<td>Alfisols</td>
<td>0.255</td>
<td>6.5</td>
</tr>
<tr>
<td>Ultisols</td>
<td>0.864</td>
<td>21.8</td>
</tr>
<tr>
<td>Oxisols</td>
<td>0.727</td>
<td>18.4</td>
</tr>
<tr>
<td>Histosols</td>
<td>0.270</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Source: Adapted from Ref. 7.
<table>
<thead>
<tr>
<th>Depth (m) (horizon)</th>
<th>pH H₂O</th>
<th>pH KCl</th>
<th>OC (g kg⁻¹)</th>
<th>Clay (%)</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Al</th>
<th>CEC</th>
<th>pH 7</th>
<th>ECEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxisol (Aquic Hapludox) [10]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.2</td>
<td>4.5</td>
<td>14</td>
<td>39.9</td>
<td></td>
<td>3.7</td>
<td>1.6</td>
<td>0.32</td>
<td>0.3</td>
<td>5.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3–0.5</td>
<td>4.0</td>
<td>9</td>
<td>42.1</td>
<td></td>
<td>0.8</td>
<td>0.4</td>
<td>0.13</td>
<td>2.1</td>
<td>3.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6–0.8</td>
<td>4.1</td>
<td>3</td>
<td>45.3</td>
<td></td>
<td>0.3</td>
<td>0.4</td>
<td>0.10</td>
<td>2.9</td>
<td>3.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxisol [11]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.2</td>
<td>5.0</td>
<td>7</td>
<td>59.0</td>
<td></td>
<td>2.8</td>
<td>1.4</td>
<td>0.25</td>
<td>0.6</td>
<td>6.7a</td>
<td>5.05</td>
<td>5.05</td>
</tr>
<tr>
<td>0.3–0.6</td>
<td>4.8</td>
<td>4</td>
<td>55.0</td>
<td></td>
<td>0.4</td>
<td>0.3</td>
<td>0.08</td>
<td>1.0</td>
<td>3.2</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>0.6–0.9</td>
<td>4.7</td>
<td>2</td>
<td>53.0</td>
<td></td>
<td>0.1</td>
<td>0.2</td>
<td>0.06</td>
<td>1.2</td>
<td>2.7</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>Ultisol (clayey, kaolinitic, isothermic Humic Hapludult) [12]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.3 (Ap)</td>
<td>4.4</td>
<td>4.0</td>
<td>20</td>
<td>23.0</td>
<td>0.50</td>
<td>0.03</td>
<td>0.31</td>
<td>2.7</td>
<td>11.9</td>
<td>3.54</td>
<td>3.54</td>
</tr>
<tr>
<td>0.3–0.6 (Bt1)</td>
<td>4.3</td>
<td>3.7</td>
<td>8</td>
<td>40.2</td>
<td>0.50</td>
<td>0.05</td>
<td>0.15</td>
<td>3.9</td>
<td>13.1</td>
<td>4.60</td>
<td>4.60</td>
</tr>
<tr>
<td>0.6–1.1 (Bt2)</td>
<td>4.4</td>
<td>3.5</td>
<td>3</td>
<td>40.7</td>
<td>0.63</td>
<td>0.08</td>
<td>0.03</td>
<td>2.6</td>
<td>9.2</td>
<td>3.34</td>
<td>3.34</td>
</tr>
<tr>
<td>Ultisol (fine, parasesquic, mesix Xeric Haplohumult) [13]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.1 (A1)</td>
<td>5.1</td>
<td>52</td>
<td>54.2</td>
<td></td>
<td>12.1</td>
<td>3.8</td>
<td>1.1</td>
<td>1.1</td>
<td>27.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2–0.4 (B1)</td>
<td>4.7</td>
<td>11</td>
<td>65.0</td>
<td></td>
<td>4.6</td>
<td>2.4</td>
<td>0.2</td>
<td>0.2</td>
<td>17.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8–1.2 (B31)</td>
<td>4.4</td>
<td>5</td>
<td>79.0</td>
<td></td>
<td>1.7</td>
<td>1.5</td>
<td>0.1</td>
<td>0.1</td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andisol (medial, isothermic Acrudoxic Hapludand) [12]</td>
<td>0–0.3 (A1)</td>
<td>4.7</td>
<td>4.6</td>
<td>42</td>
<td>0.55</td>
<td>0.09</td>
<td>0.06</td>
<td>1.20</td>
<td>26.8</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>0.3–0.6 (Bw1)</td>
<td>4.6</td>
<td>4.8</td>
<td>15</td>
<td>0.50</td>
<td>0.08</td>
<td>0.07</td>
<td>0.30</td>
<td>29.5</td>
<td>0.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9–1.9 (Bw3)</td>
<td>4.3</td>
<td>5.0</td>
<td>5</td>
<td>0.50</td>
<td>0.03</td>
<td>0.03</td>
<td>0.50</td>
<td>26.9</td>
<td>1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andisol (Histic Durauquand) [13]</td>
<td>0–0.2 (A1)</td>
<td>4.7</td>
<td>106</td>
<td>5.8</td>
<td>5.7</td>
<td>0.6</td>
<td>0.6</td>
<td>48.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2–0.4 (A2)</td>
<td>5.0</td>
<td>68</td>
<td>1.3</td>
<td>0.8</td>
<td>0.2</td>
<td>0.2</td>
<td>42.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4–0.6 (Bw)</td>
<td>5.7</td>
<td>39</td>
<td>3.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>28.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alfisol (fine-silty, mixed, mesic Typic Endoaqualf) [13]</td>
<td>0–0.1 (A1)</td>
<td>5.3</td>
<td>18</td>
<td>16.9</td>
<td>6.2</td>
<td>1.8</td>
<td>0.8</td>
<td>12.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3–0.4 (B1t)</td>
<td>5.1</td>
<td>3</td>
<td>26.9</td>
<td>9.4</td>
<td>3.6</td>
<td>0.7</td>
<td>16.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6–0.8 (B21t)</td>
<td>5.5</td>
<td>3</td>
<td>34.1</td>
<td>16.0</td>
<td>8.6</td>
<td>0.9</td>
<td>26.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alfisol (fine-loamy, siliceous, semiactive, thermic Typic Paleudalf) [13]</td>
<td>0–1 (Ap)</td>
<td>5.2</td>
<td>21.7</td>
<td>1.6</td>
<td>1.3</td>
<td>0.3</td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1–0.8 (B21t)</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8–1.1 (B22t)</td>
<td>5.2</td>
<td>23.2</td>
<td>1.1</td>
<td>1.4</td>
<td>0.3</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* At pH 6.0.
Andisols, which are most commonly not very acidic, are dominated by amorphous minerals (allophane and imogolite), organic matter, and variable charge. They have very high contents of organic matter in the surface horizon, with good to excellent physical properties down the profile. The acidic Andisols are found mainly in hot, humid regions and can become quite acid, with low basic cation content (Acrudoxic Hapludand) (Table 5).

In contrast to Ultisols, Alfisols are much less highly weathered, with only some being acidic. They usually exhibit increasing silicate clay content (mainly 2:1 clay minerals), basic cation status, and pH with depth. In Australia, many naturally nonacidic Alfisols have become acidic as a result of anthropogenic sources of acidity (see Chapters 4 and 5).

### 3.1.2 Acid Sulfate Soils

These soils, which cover 24 million ha worldwide, usually fall in the Inceptisol (Gleysoils, Rankers, Cambisols) and Entisol (Fluvisols, Gleysoils, Regosols, Arenosols) Orders and are found mostly in the delta areas of the great rivers. Prior to drainage, they have a neutral reaction as unripe sulfidic clays, but they become extremely acidic when drained (raw acid sulfate soils) due to the oxidation of reduced sulfur compounds (FeS$_x$) to sulfuric acid. After complete oxidation of the S compounds and dissipation of the sulfuric acid, which often contaminates adjacent water bodies, sulfate soils remain strongly acid (ripe acid sulfate soils). Both raw and ripe varieties contain high levels of exchangeable Al$^{3+}$ (dissolved by the acid) and high basic cation status (from their riverine origin). An example of a ripe acid sulfate soil (Typic Sulfaquept) is presented in Table 6. The pH of acid sulfate often decreases with depth, reflecting the stronger oxidizing conditions near the surface. Texture is variable, depending on the nature of the alluvial parent material. The intensity and extent of the acidity produced can be controlled by manipulation of the water table.

### 3.1.3 From Parent Materials Poor in Basic Cations

These soils occur in the Spodosol (Podzols), Histosol (Histosols), and Entisol (Fluvisols, Gleysoils, Regosols, Arenosols) Orders and are usually derived from organic, siliceous or basic cation–poor organic parent materials (Table 7).

Spodosols occur mainly in temperate regions on extremely basic cation–poor, unbuffered, coarse-textured parent materials. The spodic horizon (Bh) forms as a result of the translocation of basic cations, iron, and organic matter from the surface horizons, which, as a result, become extremely acid.

Histosols, which have very high organic matter contents, are usually acidic to strongly acidic depending on inputs of basic cations from surrounding mineral soils. They have very high CEC values due to the highly charged nature of organic matter. The acidity is due mainly to the H$^+$ ions, with the Al$^{3+}$ ions making up
<table>
<thead>
<tr>
<th>Depth (m) (Horizon)</th>
<th>pH H₂O</th>
<th>pH KCl</th>
<th>OC (g kg⁻¹)</th>
<th>Clay (%)</th>
<th>Exchangeable cations (cmolc kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Inceptisol (sandy-skeletal, mixed, mesic Typic Dystrochrept) [13]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–01 (A1)</td>
<td>4.1</td>
<td>55</td>
<td>3.0</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2–0.5 (B22)</td>
<td>5.1</td>
<td>7</td>
<td>2.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>0.5–0.7 (B23)</td>
<td>5.2</td>
<td>2</td>
<td>1.8</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Inceptisol (Typic Sulfaquept) [14]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.05</td>
<td>2.9</td>
<td>2.8</td>
<td>78</td>
<td>0.7</td>
<td>4.4</td>
</tr>
<tr>
<td>0.15–0.25</td>
<td>3.5</td>
<td>3.2</td>
<td>73</td>
<td>0.1</td>
<td>2.6</td>
</tr>
<tr>
<td>0.35–0.45</td>
<td>3.2</td>
<td>2.8</td>
<td>13</td>
<td>0.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>
### TABLE 7  Chemical Properties of Representative Spodosols, Histosols, and Entisols

<table>
<thead>
<tr>
<th>Depth (m) (Horizon)</th>
<th>pH H₂O</th>
<th>PH KCl</th>
<th>OC (g kg⁻¹)</th>
<th>Clay (%)</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Na</th>
<th>CEC</th>
<th>pH 7</th>
<th>ECEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spodosol (sandy, siliceous, isohyperthermic Grossarenic Entic Haplohumod) [13]</td>
<td>0–0.2 (A11)</td>
<td>4.0</td>
<td>3.5</td>
<td>28.8</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>0.0</td>
<td>0.4</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>1.0–1.5 (A24)</td>
<td>4.3</td>
<td>3.8</td>
<td>0</td>
<td>29.2</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>1.7–1.9 (B12h)</td>
<td>4.5</td>
<td>3.7</td>
<td>5</td>
<td>38.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.0</td>
<td>3.3</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Spodosol (sandy, siliceous, thermic Aeric Alaquod) [13]</td>
<td>0–0.2 (A)</td>
<td>3.4</td>
<td>58</td>
<td>0.4</td>
<td>0.4</td>
<td>1.0</td>
<td>0.2</td>
<td>0.0</td>
<td>16.6</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>0.2–0.2 (E)</td>
<td>3.9</td>
<td>3</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>1.1</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>0.3–0.4 (Bh)</td>
<td>4.0</td>
<td>26</td>
<td>3.4</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>12.4</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Histosol (Dysic Typic Cryohemist) [13]</td>
<td>0–0/2 (OiL31)</td>
<td>3.9</td>
<td>475</td>
<td>19.1</td>
<td>6.4</td>
<td>3.0</td>
<td>1.0</td>
<td>95.5</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2–0.5 (OAL32)</td>
<td>4.6</td>
<td>476</td>
<td>53.1</td>
<td>12.5</td>
<td>0.7</td>
<td>0.9</td>
<td>149.9</td>
<td>67.2</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5–1.3 (OA233)</td>
<td>4.2</td>
<td>449</td>
<td>119.4</td>
<td>29.3</td>
<td>0.9</td>
<td>0.9</td>
<td>160.5</td>
<td>39.9</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Histosol (very-fine, mixed, evic, isohyperthermic Terric Troposaprist) [13]</td>
<td>0–0.1 (OA1)</td>
<td>5.5</td>
<td>4.7</td>
<td>28</td>
<td>6.4</td>
<td>2.0</td>
<td>7.2</td>
<td>1.2</td>
<td>69.8</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td>0.1–0.4 (OA2)</td>
<td>5.0</td>
<td>4.4</td>
<td>14.9</td>
<td>4.1</td>
<td>2.5</td>
<td>0.0</td>
<td>0.5</td>
<td>36.6</td>
<td>22.0</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>0.4–0.8 (OA3)</td>
<td>5.1</td>
<td>4.7</td>
<td>15.8</td>
<td>3.8</td>
<td>2.5</td>
<td>0.0</td>
<td>0.5</td>
<td>31.9</td>
<td>22.6</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Entisol (mesic, uncoated Typic Quartzipsamment) [13]</td>
<td>0.01 (A1/B1)</td>
<td>3.4</td>
<td>17</td>
<td>2.0</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>1.0</td>
<td>0.2</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>0.2–0.5 (B23)</td>
<td>4.3</td>
<td>4.4</td>
<td>2</td>
<td>6.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5–0.7 (B24v)</td>
<td>4.4</td>
<td>4.3</td>
<td>1</td>
<td>3.9</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Entisol (sandy-skeletal, mixed, mesic, Typic Udorthent) [13]</td>
<td>0–0.2 (Ap)</td>
<td>5.0</td>
<td>4.3</td>
<td>28</td>
<td>5.1</td>
<td>1.6</td>
<td>0.1</td>
<td>0.2</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3–0.4 (B22)</td>
<td>5.3</td>
<td>4.6</td>
<td>6</td>
<td>2.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6–0.9 (2C2)</td>
<td>5.7</td>
<td>4.8</td>
<td>1</td>
<td>1.2</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
only a small proportion of the acidity in most Histosols. Some Histosols in fens (unforested) and swamps (forested) can have pH\textsubscript{H\textsubscript{2}O} values in the neutral range (6–7.5). Entisols are coarse-textured soils that become acid during weathering due to the lack of buffering capacity (very low CEC) within the soil.

### 3.2 Anthropogenically Derived Acid Soils

#### 3.2.1 From Acid Deposition

Combustion of fossil fuels over the past two centuries has acidified rainfall with sulfuric and nitric acids in many areas of the world (see Chapter 4). In addition, NH\textsubscript{x} from livestock and industrial sources can have a marked effect on topsoil acidification when the ammoniacal nitrogen after deposition is oxidized to nitrate, which is then leached from the topsoil [15]. There is also evidence that volcanic emissions of SO\textsubscript{2} and HCl can contribute to acid precipitation [16].

Long-term acid deposition can have negative impacts on soils, particularly in pristine systems, such as forests, where opportunities for amelioration are minimal. This is particularly true when the atmospheric load of NH\textsubscript{x}, H\textsubscript{2}SO\textsubscript{4}, or H\textsubscript{2}NO\textsubscript{3} saturates or exceeds the demand of the ecosystem for N, which can cause changes in species diversity. For example, Sverdrup et al. [17] showed that 81% of Swedish forests are receiving greater than critical acid loads, which are projected to cause growth losses of 19% of current levels. Edges of forests are particularly vulnerable as they tend to filter off preferentially atmospheric NH\textsubscript{x} from such sources as livestock production. In Belgium, De Schrijver et al. [15] found that soil pH\textsubscript{H\textsubscript{2}O} at the edge of a Corsican pine stand downwind from an intensive livestock area was 3.1, whereas in the center of the stand it was 3.8. The edge received twice as much NH\textsubscript{4}\textsubscript{-N} as the center. In cultivated soils, such negative impacts can be readily counteracted by liming, a common agronomic practice (see Chapter 11).

Severe forest decline due to acid rain has been reported in Europe and North America on coarse-textured, poorly buffered soils where basic cation depletion and acidification can be severe. Acid depositions of 0.8–6.4 kmol H\textsuperscript{+} ha\textsuperscript{-1} year\textsuperscript{-1} have been recorded in central Europe [18]. At Rothamsted over the period 1883–1983, a soil in the wilderness area (regenerated hardwood forest), which has been unlimed and unfertilized since 1885, has become severely acidified (Table 8) as a result of acid deposition rates estimated to be 1.05, 1.67 and 3.90 kmol H\textsuperscript{+} ha\textsuperscript{-1} year\textsuperscript{-1} in 1850, 1920–1930, and 1983, respectively. Johnston et al. [19] estimated that this acidification resulted in basic cation losses equivalent to 14.0, 9.0, and 5.5 kmol Cu\textsuperscript{2+} ha\textsuperscript{-1} year\textsuperscript{-1} in 1883, 1930, and 1984, respectively. Such losses can severely reduce the fertility status of the soil, subjecting the trees to nutritional stress. On the other hand, Markewitz et al. [20] in North Carolina found that acid rain accounted for only 38% of soil acidification over a 30-year period. Although tree species can contribute to forest soil
acidification, the magnitude is small compared with that of acid deposition [15] and other factors [21].

3.2.2 From Intensively Managed Row Crop Agriculture

Under intensive agronomic row crop production, the major acidifying acid input is usually ammoniacal fertilizer N, which can rapidly acidify a soil profile if lime applications are not made. Disturbance of the C cycle and removal of alkaline products can also contribute. The acidity from ammoniacal fertilizers arises from the nitrification reaction, with the quantity of acidity produced depending on N source, extent of nitrate leaching, and uptake of N by the crop (see Chapters 2 and 3). For example, annual applications of 300 kg N ha\(^{-1}\) as urea to two crops of corn per year over 18 years caused severe acidification of an Ultisol in Nigeria [22,23] (Table 9). In addition to a substantial loss of organic C (OC), the profile has been depleted in basic cations and, with decreasing pH, increasing amounts of exchangeable Al\(^{3+}\) and Mn\(^{2+}\) (data not presented) have appeared in both top- and subsoils. High concentrations of Al\(^{3+}\) and Mn\(^{2+}\) are toxic to the crop, with Al\(^{3+}\) impairing root growth and Mn\(^{2+}\) having adverse effects on the tops. Retaining the corn residue has had a slight positive effect in stemming acidification. The type of ammoniacal source also has an effect on the rate of acidification, with ammonium sulfate having a greater acidifying effect than urea or calcium ammonium nitrate [24]. Similar results were obtained by Bouman et al. [25] in Saskatchewan, except that Mn\(^{2+}\) rather than Al\(^{3+}\) became soluble and was likely to be the main toxicant when soils were acidified by excessive fertilization.

3.2.3 From Pasture Systems

For pastures to be productive, inputs of nitrogen (and other fertilizers) are required, which often leads to acidification, the intensity of which depends on the nitrogen

---

**TABLE 8** Change in pH\(_{\text{H}_2\text{O}}\) Value with Depth on an Unlimed and Unfertilized Soil Under Woodland (Mainly Regenerated Deciduous Species) at Rothamsted over the Period 1883–1983

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>1883</th>
<th>1904</th>
<th>1965</th>
<th>1983</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.23</td>
<td>7.1</td>
<td>6.1</td>
<td>4.5</td>
<td>4.2</td>
</tr>
<tr>
<td>0.23–0.46</td>
<td>7.1</td>
<td>6.9</td>
<td>5.5</td>
<td>4.6</td>
</tr>
<tr>
<td>0.46–0.69</td>
<td>7.1</td>
<td>7.1</td>
<td>6.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*Source: Adapted from Ref. 19.*
carrier and rate of application. Long-term (1876–1984) applications of ammoniacal fertilizers to pasture systems clearly acidify the soils as demonstrated by the work of Johnston et al. [19] at Rothamsted (Table 10). On the control plot (no fertilizer) and no-nitrogen plots (received other fertilizers), soil pH remained fairly constant, with the slight increase between 1856 and 1923 being due to small applications of chalk (lime) between 1881 and 1896. There was a slight downward drift

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Depth (m)</th>
<th>pH H₂O</th>
<th>OC (g kg⁻¹)</th>
<th>Exchangeable cations (cmolₑ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Bush fallow (control)</td>
<td>0–0.1</td>
<td>6.2</td>
<td>19</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>0.1–0.2</td>
<td>6.2</td>
<td>6</td>
<td>4.7</td>
</tr>
<tr>
<td>Corn (residue removed)</td>
<td>0–0.1</td>
<td>4.5</td>
<td>6</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>0.1–0.2</td>
<td>4.5</td>
<td>5</td>
<td>2.1</td>
</tr>
<tr>
<td>Corn (residue retained)</td>
<td>0–0.1</td>
<td>4.8</td>
<td>10</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>0.1–0.2</td>
<td>4.7</td>
<td>6</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*Source: Adapted from Ref. 22.*

<table>
<thead>
<tr>
<th>Nitrogen rate (kg N ha⁻¹ year⁻¹)</th>
<th>Depth (m)</th>
<th>1876</th>
<th>1923</th>
<th>1959</th>
<th>1976</th>
<th>1984</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0–0.23</td>
<td>5.3</td>
<td>5.7</td>
<td>5.2</td>
<td>5.3</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.23–0.46</td>
<td>6.1</td>
<td>6.2</td>
<td>5.3</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>0–0.23</td>
<td>5.3</td>
<td>4.8</td>
<td>4.0</td>
<td>4.1</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>0.23–0.46</td>
<td>6.2</td>
<td>6.2</td>
<td>5.2</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>0–0.23</td>
<td>4.8</td>
<td>4.0</td>
<td>3.8</td>
<td>3.9</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>0.23–0.46</td>
<td>6.4</td>
<td>4.8</td>
<td>4.3</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>0–0.23</td>
<td>4.3</td>
<td>3.8</td>
<td>3.7</td>
<td>3.7</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>0.23–0.46</td>
<td>6.5</td>
<td>4.4</td>
<td>4.1</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

*Source: Data from Ref. 19.*
of topsoil pH after 1923, due largely to atmospheric depositions estimated to be about 2 kmol H⁺ ha⁻¹ year⁻¹ from the 1920s to 1984. This is also reflected in subsoil pH. On the plots receiving ammonium sulfate, there was an initial rapid decline in top- and subsoil pH, which then leveled out to an equilibrium value of about 3.6 ± 0.2 in the topsoil, with the subsoil being slightly less acid. This equilibrium topsoil pH was reached in about 50 years on the high-N treatments, whereas 100 years was required on the low-N treatments. Buffering in this soil is the result of the dissolution of Al³⁺ from aluminous minerals. Based on estimates of other acidifying processes (crop removal of basic cations and acid precipitation), the nitrification reaction and leaching of nitrate produced at least 90% of the acidity over this period. However, because nitrification is severely impeded by strong acidity, further acidification of the topsoil due to nitrification will now be minimal as shown by the lack of nitrate in the grass samples from the very acidic plots [26]. Under such conditions where atmospheric inputs constitute a large proportion of the H⁺ entering the soil, any H⁺ entering the system is likely to move straight through and continue to acidify the subsoil because of the lack of buffering by H⁺-Ca²⁺ exchange. On the other hand, the pH value of treatments receiving nitrogen in the form of nitrate increased by 0.5 to 1.0 pH units (data not shown).

![Graph showing soil pH](image)

**Figure 3** Effect of rates of calcitic limestone on soil profile acidity after 4 years under a Coastal bermudagrass (*Cynodon dactylon* [L.] Pers.) sod fertilized with NH₄NO₃ at an annual rate of 900 kg ha⁻¹. Single lime applications were made at the beginning of the experiment, except for the treatment labeled “6.7 t ha⁻¹ annually.” (From Ref. 27.)
In an experiment with Coastal bermudagrass fertilized with ammonium nitrate at a rate of 900 kg N ha$^{-1}$ year$^{-1}$ for 4 years, soil pH in the top 50 cm of soil declined markedly (Fig. 3) in the absence of lime. When sufficient lime was applied to neutralize the acidity produced and to form calcium nitrate, which can move into the subsoil, pH down the entire profile was increased due to the transfer of alkalinity from the top- to subsoil where roots assimilate more nitrate than calcium [3]. Thus, even in undisturbed pasture or grassland situations, it is possible to prevent acidification of the soil provided that adequate and timely applications of lime are made. What is important is that the topsoil should never be allowed to become acid, which requires regular applications of lime in the topsoil to neutralize the acidity.

Under grassland conditions, soil biota are very important in the cycling of nutrients. Acidification due to ammoniacal fertilizers can drastically reduce earthworm numbers and their biomass [28], resulting in the accumulation of thatch on the soil surface. Because of the lack of incorporation of these residues, decomposition and microbial mineralization are reduced.

4 RATES OF ACIDIFICATION

4.1 Pristine Systems

Johnson et al. [29] estimated the average net loss of Ca$^{2+}$ from the floor of a forest in New York to be 60 mol ha$^{-1}$ year$^{-1}$ during the period 1931 to 1984, which was much lower than more recently measured values (710 mol ha$^{-1}$ year$^{-1}$ in O horizons and 322 mol ha$^{-1}$ year$^{-1}$ in mineral horizons) in an adjacent forest from 1986 to 1990 (Table 11). They ascribed the differences to measured decreases in long-term trends in Ca$^{2+}$ deposition from rainfall in recent decades, the reason for which is not known. In the O horizon, the main contributors to acidification of the forest floor were the production and leaching of sulfate and organic anions followed by uptake of basic cations. Removal of acids occurred by leaching of H$^{+}$ and Al$^{3+}$ and by mineralization of organic matter. In the deeper mineral horizons, transfer of H$^{+}$ and Al$^{3+}$ from the surface and uptake of basic cations were the main causes of acidification, while sulfate sorption and decomposition of organic anions consumed acidity.

In various parts of Europe, declines in soil pH have been recorded partially as a result of acid precipitation [30,31] and partially as a result of changes in vegetation or the redistribution of basic cations between underlying mineral soil and the organic O horizon [30]. Rates of acidification in Sweden have ranged from 0.3 to 0.9 pH units in 55 years [32], 0.5 to 1.0 pH units in 30–50 years [31], and 0.78 pH units in 35 years [33], and in Scottish forests Billet et al. [30] found decreases in pH in organic horizons of 0.07 to 1.28 and in mineral horizons of 0.16 to 0.54 over a period of 40 years.
<table>
<thead>
<tr>
<th>Table 11: Acidification Caused by Various Factors in O Horizons and in Combined Mineral Horizons from a Spruce–Fir Forest in New York During the Period 1986–1990</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protons (mol ha</strong>⁻¹ <strong>year</strong>⁻¹)</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td><strong>O horizons</strong></td>
</tr>
<tr>
<td><strong>H⁺ produced</strong></td>
</tr>
<tr>
<td><strong>H⁺ consumed</strong></td>
</tr>
<tr>
<td><strong>Net</strong></td>
</tr>
<tr>
<td><strong>Combined mineral horizons</strong></td>
</tr>
<tr>
<td><strong>H⁺ produced</strong></td>
</tr>
<tr>
<td><strong>H⁺ consumed</strong></td>
</tr>
<tr>
<td><strong>Net</strong></td>
</tr>
</tbody>
</table>

*Source: Adapted from Ref. 29.*
4.2 Managed Systems

Agricultural production systems undergo accelerated soil acidification as a consequence of anthropogenic inputs and outputs. In this respect, the rate at which a production system acidifies is a function of the intrinsic soil properties (buffering capacity), climate, and farming practice. As discussed previously, the resultant decline in soil pH associated with agricultural production systems may be sufficient to cause moderate to severe Al\(^{3+}\) and Mn\(^{2+}\) toxicity, thereby affecting the long-term economic viability of farming systems and resulting, in some cases, in permanent degradation of the resource base. It is, therefore, of importance that the rate of acid addition to soils by these various inputs and outputs be known in order to facilitate corrective actions by the producer and society as a whole.

Rates of acid addition in agronomic production systems have been compared with those in native ecosystems and found to be significantly higher [30,34]. Soil acidification rates can be estimated as either “absolute” changes or changes relative to some control soil. Using the first method, acid addition rates are calculated from analyses of soils before and after a period of acidification [35]. This requires comparable measurements, usually separated by many years [36]. However, relative rates of acidification can be derived from survey data (e.g., fence-line contrasts) and are reported more often because of the paucity of reference data from long-term studies. A compilation of acid addition rates under various cropping and pasture production systems is presented in Table 12. The values have invariably been derived using the model of Helyar and Porter [37] that takes into account changes in the size of various pools in the N and C cycles. Rates of acid addition range from net alkalization (25.2 to 20.5 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\)) in the case of tobacco crops to significant acid additions (28 to 40 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\)) in the case of banana plantations in the wet tropics (Table 12). In the former case, net alkalization is associated with approximately 70% of the nitrogen fertilizer being in the nitrate form because ammonium-based fertilizers cause the leaf to have poor curing properties [45]. In contrast, the extremely high acidification rates recorded in banana production systems are a consequence of fertigation with high rates of ammonium-based fertilizers (average application rate of 508 kg N ha\(^{-1}\) year\(^{-1}\)), coupled with the removal of significant alkalinity in both harvested product and plant pruning following bunch removal [45].

From a strategic perspective, quantification of acid addition rates under various agronomic production systems can assist producers, extension officers, and policy makers in making decisions on the long-term impact of a production system on the resource base. For example, the introduction of a legume species and its subsequent dominance in native pasture systems in northern Australia resulted in significant acidification to depth over a period of 15 years [39]. These grazing
**Table 12** Estimated Acid Addition Rates (AARs) for a Range of Production Systems in Australia

<table>
<thead>
<tr>
<th>Production system</th>
<th>AAR range (kmol H⁺ ha⁻¹ year⁻¹)</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agroforestry</td>
<td>0.9</td>
<td>Eucalypt forest compared with unimproved pasture</td>
<td>38</td>
</tr>
<tr>
<td>Grazed <em>Stylosanthes</em>-based extensive pasture</td>
<td>0–3.5</td>
<td>Legume-based extensive pasture production systems in the wet/dry tropics</td>
<td>39</td>
</tr>
<tr>
<td>Grazed clover pasture</td>
<td>1.2–3.6</td>
<td>Grazed white clover/paspalum grass pasture in the wet subtropics</td>
<td>40</td>
</tr>
<tr>
<td>Grazed clover pastures</td>
<td>0.8–4.4</td>
<td>Subterranean clover/annual or perennial grass pasture systems of the temperate highlands</td>
<td>39–44</td>
</tr>
<tr>
<td>Pasture cut for hay</td>
<td>1.0–6.0</td>
<td>Grass cut and removed without nitrogen fertilizer in the wet tropics</td>
<td>45</td>
</tr>
<tr>
<td>Pasture cut for hay</td>
<td>10.0–11.0</td>
<td>Nitrogen-fertilized grass pasture cut and removed for hay in the wet tropics</td>
<td>45, 46</td>
</tr>
<tr>
<td>Pasture cut for hay</td>
<td>0.6–1.0</td>
<td>Annual pasture grown under temperate conditions</td>
<td>47</td>
</tr>
<tr>
<td><em>Stylosanthes</em> seed production systems</td>
<td>10.6</td>
<td>Irrigated seed production system in the dry tropics</td>
<td>39</td>
</tr>
<tr>
<td>Cereals</td>
<td>0.9–4.6</td>
<td>Continuous wheat with and without nitrogen fertilizers</td>
<td>48</td>
</tr>
<tr>
<td>Lupins</td>
<td>12.5</td>
<td>Continuous lupin monoculture (17 years) grown under a temperate climatic regime</td>
<td>48</td>
</tr>
<tr>
<td>Sugarcane</td>
<td>2.8–4.7</td>
<td>Sugarcane monocultures grown under a wet tropical and subtropical climate</td>
<td>45</td>
</tr>
<tr>
<td>Tobacco</td>
<td>−5.2 to −0.5</td>
<td>Tobacco monoculture grown under irrigation in the wet/dry tropics</td>
<td>41</td>
</tr>
<tr>
<td>Banana</td>
<td>28–40</td>
<td>Banana plantation crop in the wet tropics</td>
<td>41</td>
</tr>
<tr>
<td>Grapes</td>
<td>1.3–2.5</td>
<td>Vineyard in the subtropics</td>
<td>41</td>
</tr>
</tbody>
</table>
systems are characterized as low input and extensive in nature; consequently, con-
ventional intervention strategies to ameliorate acidification through prophylactic
applications of lime are uneconomic. Therefore, an alternative approach of iden-
tifying soils that are predisposed to accelerated acidification would assist land
managers in making informed decisions on where to establish improved
*Stylosanthes*-based native pastures. This has been done for an area in northern
Queensland (the Dalrymple Shire) where a comprehensive land resource assess-
ment had been undertaken [53]. Using intrinsic soil characteristics (silt, clay, and
organic carbon content), a pedotransfer function was developed to predict pH
buffer capacity [39]. By modifying the function of Helyar and Porter [37] and us-
ing a constant rate of net acid input (3.5 kmol H$^+$ ha$^{-1}$ year$^{-1}$), the number of
years for a soil association to fall from its current pH to 5.5 was estimated and de-
picted in a map using geographic information systems (GIS) technology (Fig. 4).
Quite clearly, a significant proportion of the soils within the Dalrymple Shire are
predisposed to accelerated soil acidification, and therefore the development of
such risk maps would assist land managers in their decision-making process. By
differentiating soils that are predisposed to accelerated acidification, a manager
may strategically establish *Stylosanthes* in areas where the soils have the capacity
to buffer acid inputs. In contrast, if managers do not have suitable areas of soils
with high buffering capacity, they are aware of the risk of accelerated acidifica-
tion and therefore may implement management strategies that minimize the risk
of *Stylosanthes* dominance [39].

<table>
<thead>
<tr>
<th>Production system</th>
<th>AAR range (kmol H$^+$ ha$^{-1}$ year$^{-1}$)</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat/pasture rotation</td>
<td>0.2–5.1</td>
<td>Selected rotation studies of varying age</td>
<td>36, 43, 45</td>
</tr>
<tr>
<td>Wheat/lupin rotations</td>
<td>0.15–4.1</td>
<td>Rotations of varying age</td>
<td>43, 46–48</td>
</tr>
<tr>
<td>Cereal/clover pasture</td>
<td>0.15–0.92</td>
<td>Cereal/subclover pasture rotations under temperate climatic conditions</td>
<td>45, 48</td>
</tr>
<tr>
<td>Wheat/fallow rotation</td>
<td>−0.5–0.4</td>
<td>Wheat fallow rotation with no nitrogen applied</td>
<td>36</td>
</tr>
<tr>
<td>Irrigated rice/wheat/pasture rotations</td>
<td>7.9–10.4</td>
<td>Rice/wheat/pasture grown under irrigation in a temperate environment</td>
<td>36</td>
</tr>
</tbody>
</table>
Figure 4  Acidification risk map for the Dalrymple Shire based on the time required for the soil pH_{\text{H}_{2}O} to decline to 5.5.
5 CONCLUSIONS

Topsoils affected by acidity account for 30% of the total ice-free area of the world with the Americas, Africa, and Asia accounting for the largest portions. Approximately 75% of these areas are also affected by subsoil acidity. As expected, intensely weathered soils (Oxisols and Ultisols) account for the largest areas but anthropogenic acidification resulting from the use of ammoniacal fertilizers and atmospheric fallout is of great importance in both cultivated and natural systems. Rates of acidification can vary from 0.7 kmol H⁺ ha⁻¹ year⁻¹ in pristine systems to as high as 40 kmol H⁺ ha⁻¹ year⁻¹ in production systems receiving high rates of ammoniacal N fertilizers.

REFERENCES


Role of Carbon, Nitrogen, and Sulfur Cycles in Soil Acidification

Nanthi S. Bolan and Mike J. Hedley
Massey University, Palmerston North, New Zealand

1 INTRODUCTION

Under areas where rainfall exceeds evapotranspiration, soil acidification is an ongoing process that can be either accelerated by the activity of plants, animals, and humans or slowed down by careful management practices [1,2]. In areas that remain unaffected by industrial pollution, soil acidification is mainly caused by the release of protons (H\(^+\)) during the transformation and cycling of carbon (C), nitrogen (N), and sulfur (S) in the soil–plant–animal system [3,4]. Under managed systems much of the accelerated soil acidification is caused by increasing N and S inputs into the farming system (Table 1). For example, in areas of Australia where legumes have been grown continuously for more than 30 years, the soil pH has decreased by about one unit [5–10]. Similarly, in New Zealand, intensively managed legume-based dairy pastures require applications of approximately 2.5 tons of lime per ha every 6 years [11,12] to neutralize acidity mostly generated through loss of N from an accelerated N cycle.

Soil acidification caused by increases in C, N, and S input to a managed farming system can have adverse impacts where soils are unable to buffer against pH decrease. For example, in some parts of Australia, continuous legume cultivation and inappropriate nitrogenous fertilizer use have generated sufficient soil...
acidity that wheat cultivation has had to be abandoned due to aluminum and manganese toxicity [13–15]. Soil acidification enhances the mobilization of toxic metals in soils, resulting in increased uptake by plants. Some of these toxic metals subsequently reach the food chain through plant products and grazing animals [16]. In this chapter, we first examine the various soil, plant, and animal processes that generate acid (protons; H\(^+\) ions) during the cycling of C, N, and S. Second, the effects of these acid generation processes on soil acidification for legume-based pastures are examined. Third, methods to minimize soil acidification from C, N, and S cycles are proposed.

### 2 NUTRIENT CYCLING PROCESSES THAT GENERATE ACID OR ALKALI

The most significant proton (H\(^+\)) and hydroxyl ion (OH\(^-\)) generating processes occur during the cycling of C, N, and S (Table 2). In the case of the C cycle, dis-

<table>
<thead>
<tr>
<th>Agricultural system</th>
<th>Total acidity (kmol H(^+) ha(^{-1}) year(^{-1}))</th>
<th>Percent contribution</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grazed pasture</td>
<td>3.46–4.22</td>
<td>49–60 41–51</td>
<td>1</td>
</tr>
<tr>
<td>Intensive dairy pasture</td>
<td>11.4</td>
<td>31 69</td>
<td>2</td>
</tr>
<tr>
<td>Hill country pasture</td>
<td>8.60</td>
<td>17 83</td>
<td></td>
</tr>
<tr>
<td>Verano <em>Stylosanthes</em></td>
<td>1.08</td>
<td>100 0</td>
<td></td>
</tr>
<tr>
<td>Pasture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilized</td>
<td>1.42</td>
<td>65 35</td>
<td></td>
</tr>
<tr>
<td>Unfertilized</td>
<td>0.16</td>
<td>100 0</td>
<td></td>
</tr>
<tr>
<td><em>Leucaena</em> based pasture</td>
<td>1.03</td>
<td>84 16</td>
<td>8</td>
</tr>
<tr>
<td>Continuous wheat</td>
<td>0.35</td>
<td>98 2.0</td>
<td>10</td>
</tr>
<tr>
<td>1 Pasture–1 cereal rotation</td>
<td>0.41</td>
<td>19 81</td>
<td></td>
</tr>
<tr>
<td>2 Pasture–1 cereal rotation</td>
<td>0.82</td>
<td>39 61</td>
<td></td>
</tr>
<tr>
<td>Continuous pasture</td>
<td>0.92</td>
<td>25 75</td>
<td></td>
</tr>
<tr>
<td>Hill country pasture</td>
<td>1.05–3.83</td>
<td>38–41 62–59</td>
<td>12</td>
</tr>
<tr>
<td>P trial—pasture</td>
<td>2.7–3.21</td>
<td>18–56 44–82</td>
<td>74</td>
</tr>
<tr>
<td>Subclover</td>
<td>2.0</td>
<td>65 35</td>
<td></td>
</tr>
<tr>
<td><em>Phalaris</em></td>
<td>1.36</td>
<td>0.2 99</td>
<td></td>
</tr>
<tr>
<td>Lupin</td>
<td>0.37</td>
<td>47 53</td>
<td>91</td>
</tr>
<tr>
<td>Lupin</td>
<td>0.19</td>
<td>— 100</td>
<td></td>
</tr>
<tr>
<td>Lupin</td>
<td>0.47</td>
<td>38 62</td>
<td></td>
</tr>
<tr>
<td>Cereal—annual pasture</td>
<td>0.19–0.23</td>
<td>100 0</td>
<td>96</td>
</tr>
</tbody>
</table>
solution of CO₂ to form carbonic acid in soil solution and synthesis and dissociation of carboxylic acids produced by plants and microorganisms are the two main sources of H⁺ ions. The assimilation of CO₂ into carboxylic acids (including amino and fatty acids) in higher plants indirectly acidifies the soil explored by their roots. Dissociation of some newly synthesized organic acids creates negatively charged organates (e.g., RCOO⁻) and H⁺ ions. Charge-balancing basic cations from the rooting media are exchanged for the H⁺ ions (see Sec. 2.1.1 for more details) to maintain both cytoplasmic pH buffering and internal plant charge balance. During plant senescence, organates (e.g., RCOO⁻) are mineralized, generating HCO₃⁻ ions that neutralize protons. Storage of organic matter in soil or removal of plant products prevents the cycling being completed. Carbon commonly enters and leaves the terrestrial part of the C cycle as CO₂, particularly if growth and decomposition processes are in equilibrium. For ecosystems that have ap-

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction equation</th>
<th>H⁺ production (mol mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon cycle</td>
<td>Dissolution of carbon dioxide</td>
<td>CO₂ + H₂O → H₂CO₃ → H⁺ + HCO₃⁻</td>
</tr>
<tr>
<td></td>
<td>Synthesis of organic acid</td>
<td>Organic C → RCOOH → RCOO⁻ + H⁺</td>
</tr>
<tr>
<td>Nitrogen cycle</td>
<td>N fixation</td>
<td>N₂ + H₂O + 2R—OH → 2R—NH₃ + 1.5 O₂</td>
</tr>
<tr>
<td></td>
<td>Mineralization of organic N</td>
<td>RNH₂ + H⁺ + H₂O → R—OH + NH₄⁺</td>
</tr>
<tr>
<td></td>
<td>Urea hydrolysis</td>
<td>(NH₂)₂CO + 3H₂O → 2NH₄⁺ + 2OH⁻ + CO₂</td>
</tr>
<tr>
<td></td>
<td>Ammonium assimilation</td>
<td>NH₄⁺ + R—OH → R═NH₂ + H₂O + H⁺</td>
</tr>
<tr>
<td></td>
<td>Ammonia volatilization</td>
<td>NH₃ + OH⁻ → NH₄↑ + H₂O</td>
</tr>
<tr>
<td></td>
<td>Nitrification</td>
<td>NH₄⁺ + 2O₂ → NO₃⁻ + H₂O + 2H⁺</td>
</tr>
<tr>
<td></td>
<td>Nitrate assimilation</td>
<td>NO₃⁻ + 8H⁺ + 8e⁻ → NH₄⁺ + 2H₂O + 2OH⁻</td>
</tr>
<tr>
<td></td>
<td>Denitrification</td>
<td>2NO₃⁻ + 2H⁺ → N₂ + 2.5O₂ + H₂O</td>
</tr>
<tr>
<td>Sulfur cycle</td>
<td>Mineralization of organic S</td>
<td>Organic S + 1.5O₂ + H₂O → SO₄²⁻ + 2H⁺</td>
</tr>
<tr>
<td></td>
<td>Assimilation of sulfate</td>
<td>SO₄²⁻ + 8H⁺ + 8e⁻ → SH₂ + 2H₂O + 2OH⁻</td>
</tr>
<tr>
<td></td>
<td>Oxidation of elemental sulfur</td>
<td>2S²⁻ + 2H₂O + 3O₂ → 2SO₄²⁻ + 4H⁺</td>
</tr>
</tbody>
</table>
proached this steady state with respect to C-induced acid- and alkali-generating transformations, there is little net acidification caused by the C cycle.

In the case of the N and S cycles, mineralization and oxidation of organic N and S result in the production of H⁺ ions. However, this is balanced by OH⁻ generated through uptake and assimilation of NO₃⁻-N and SO₄²⁻-S by plants and microorganisms [17]. Leaching of SO₄²⁻ and NO₃ with charge-balancing basications (Ca²⁺, Mg²⁺, K⁺, or Na⁺), rather than the H⁺ ions generated during oxidation, results in permanent acidity remaining in the soil [18]. This is reflected in a decrease in pH in soils with low pH buffer power.

Commonly, the amount of S cycling within an ecosystem is roughly one tenth of the amount of N; in general, therefore, if the turnover time of S in a cycle is similar to that of N, N cycling will generate approximately 10 times the quantities of H⁺ and OH⁻ ions generated during S cycling [19]. In addition, the extent of soil acidification resulting from a unit of N and S may differ due to differences in the form of element entering and leaving the system and the pathways involved. For example, N may enter a managed terrestrial ecosystem as N₂ gas, NH₄⁺ in rainfall, or N fertilizer. It can leave as N₂, N₂O, NO₃⁻, NH₃, or RNH₂ in products. As discussed later, N leaving in a form with more negative charge than the form of N entering the cycle acidifies the soil, whereas N leaving in a form with less negative charge than the form of N entering the cycle makes the soil more alkaline. In the former case, the charge balance in the soil is achieved through the release of H⁺ ions, leading to soil acidification, whereas in the later case the charge balance is achieved through the release of OH⁻ or HCO₃⁻ ions, leading to soil alkalization. Sulfur in aerobic soils commonly enters as SO₄²⁻ in fertilizers and rainfall and leaves as SO₄²⁻ in drainage or RSH₂ in plant product, having little impact on the amount of acid it leaves in the soil. Difference in leaching of SO₄²⁻ and NO₃⁻ in the soil also contributes to the difference in the amount of acid produced by these two elements in soils. Some soils, particularly highly weathered soils, strongly adsorb SO₄²⁻ but not NO₃⁻. Thus, SO₄²⁻ leaching is reduced [20] and the potential for greater recycling of S by plant uptake exists. In the case of NO₃⁻, however, most soils have little ability to retain NO₃⁻, making it susceptible to leaching [21–23]. Thus, NO₃⁻ leaching in legume systems (N input as N₂ gas) and ammonium-fertilized systems will leave the soil with permanent acidity. These aspects are covered subsequently in more detail.

We think it is easier to understand soil acidification if we break it into two parts: (1) biological processes that generate acid in soils and (2) processes that interrupt or uncouple nutrient cycling that leave acid in soils. The processes involved in the generation of H⁺ and OH⁻ ions during C, N, and S cycling in soil can be grouped into two main categories: plant induced—the uptake and assimilation of C, N, and S; and soil induced—the transformation of C, N, and S in soil. These processes are discussed briefly in the following section.
2.1 Plant-Induced Processes

2.1.1 Carbon Assimilation

In higher plants, carbon is first assimilated as carbohydrates during the photosynthetic process. The subsequent metabolism of the photosynthates results in the synthesis of organic acids, such as malic and oxalic acids (process 4 in Fig. 1). At the cytoplasmic pH of the plants (pH ≈ 7.2 to 7.4), some of the carboxyl groups of simple acids, amino acids, proteins, and more complex structural carbohydrates (e.g., pectins) dissociate (processes 5 and 8 in Fig. 1) to produce H⁺ ions [24].

The excess H⁺ ions are disposed of by neutralization resulting from decarboxylation, by transport into the vacuole, or by transport via the phloem into the roots and thence into the soil solution. If the excess H⁺ ions are not removed physically or chemically (neutralization) from the cytoplasm, they lead to pH decrease in the cytoplasm [25]. Cytoplasmic pH regulation may most generally be achieved by transport of excess H⁺ ions out of the cytoplasm. The sink to which these ions are transported is typically the external solution. Excretion into the surrounding aqueous medium is the usual means of pH regulation in aqueous plants. In the case of land plants, some species counteract the change in cytoplasm pH by excreting H⁺ ions into the soil solution and at the same time taking in basic nutrient cations to balance the charge (process 9 in Fig. 1). Thus, the soil becomes more acidic [26].

2.1.2. Uptake and Assimilation of Nitrogen

Plants take up N in three main forms—as an anion (nitrate, NO₃⁻), as a cation (ammonium, NH₄⁺), or as a neutral N₂ molecule (N₂ fixation, in legumes only). Depending on the form of N taken up and the mechanism of assimilation in the plant, excess uptake of cations or anions may occur [27–30]. To maintain charge balance during the uptake process, H⁺, OH⁻, or HCO₃⁻ ions must pass out of the root into the surrounding soil. The H⁺ ions may be derived from the dissociation of organic acids within the cell and OH⁻ ions from the decarboxylation of organic acid anions. It has been shown that whereas the uptake of NH₄⁺ and fixation of N₂ result in a net release of H⁺ ions (process 6 in Fig. 1), uptake of NO₃⁻ can result in a net release of OH⁻ ions (process 1 in Fig. 1) [31–36].

**Nitrogen Fixation.** In the case of N₂ fixation, the neutral N₂ can be assimilated into protein, and no charge imbalance is generated across the soil–root boundary (process 7 in Fig. 1). Many legumes, however, commonly export H⁺ ions into their rhizosphere when actively fixing N₂ [27,37–39]. The generation of this acidity is dependent on the chemical nature of compounds that are formed during C and N assimilation (e.g., amino acids). Part of the H⁺ ions generated within the legume root comes from the dissociation of the carboxyl groups of amino acids (process 8 in Fig. 1). The acidity generated by fixation of N₂ in
FIGURE 1 Processes of nitrogen and carbon assimilation in plants that influence rhizosphere acidity. The encircled numbers represent (1) nitrate assimilation in roots, (2) xylem transport of nitrate to shoot, (3) nitrate assimilation in shoot, (4) synthesis of organic acid from sugars, (5) dissociation of organic acid (e.g., malic acid) in the shoot, (6) assimilation of ammonium in roots, (7) biological nitrogen fixation, (8) dissociation of amino acid, and (9) dissociation of organic acid (e.g., malic acid) in the root.
legumes has been found to be equivalent to the excess uptake of cations over anions by the plant and to vary from 0.2 to 0.7 mole H\(^+\) per mole of fixed N [37–40]. The reason for the generation of acidity, even when no ionic species of N are taken up by the plant, is that basic cations are imported into the legume in exchange for H\(^+\) ions generated during C assimilation into carboxylic acids. In order to maintain pH balance, these H\(^+\) ions are subsequently exported from the roots, generating acidity in the soil.

Some tropical legumes, however, do not apparently acidify their rhizospheres as much as do temperate legumes when actively fixing N\(_2\) [41]. Part of the reason for this is that their NH\(_3\) assimilation products appear to be ureides (allantoin and allantoic acid) that have high pK\(_a\) values (e.g., allantoin pK\(_a\) 8.96) and are therefore unlikely to dissociate and donate H\(^+\) ions at cytoplasmic and xylem pH values. Thus, we find that many tropical legumes accumulate less cations than temperate legumes [42].

The amount of H\(^+\) ions released during N\(_2\) fixation is really a function of C assimilation and therefore depends mainly on the form and amount of amino acids and organic acids synthesized within the plant [41]. The rate of acidification by a number of temperate and tropical legumes has been examined in many studies [39,43–45], as measured by uptake of excess cations over anions. Although the excess cation values varied widely between the legume species, removal of plant biomass from the field, rather than concentration of excess cations, was considered to be the major determinant of legume-induced soil acidification.

Ammonium and Nitrate Assimilation. When ammonium (NH\(_4^+\)) assimilation occurs in roots, deprotonation of NH\(_4^+\) (the deprotonation product is represented as amide nitrogen R—NH\(_2\)) releases 1 mole of H\(^+\) per mole of NH\(_4^+\) (process 6 in Fig. 1) [Eq. (1)]. Additional small amounts of H\(^+\) ions are generated during the assimilation of R—NH\(_2\) into amino acids and proteins that have isoelectric pH values lower than the cytoplasmic pH. For example, Breteler [46] observed that sugar beet plants supplied with ammoniacal nitrogen released 1.1 to 1.2 H\(^+\) ions per NH\(_4^+\) ion taken up. The specific reason for this additional H\(^+\) ion input is that, in most plants, NH\(_3\) is initially assimilated into the dicarboxylic amino acids, aspartate and glutamate [47,48]. Aspartate and glutamate are strong carboxylic acids that dissociate to produce H\(^+\) ions at cytoplasm and xylem pH values. In order to maintain a pH balance, the plant exports the dissociated H\(^+\) ions in exchange for cations from the rooting media. For NH\(_4^+\) assimilation to occur in shoots, NH\(_4^+\) is transported up the xylem with a companion malate ion [24]. The H\(^+\) ions released when NH\(_4^+\) is deprotonated in the shoots can be neutralized by OH\(^-\) ions generated during decarboxylation of malate; alternatively, undissociated malic acid may be formed and translocated to the root. Maintenance of cytoplasmic pH by this process is known as the “biochemical” or “malate” pH stat [24,49].

\[
\text{NH}_4^+ + \text{R—OH} \rightarrow \text{R—NH}_2 + \text{H}_2\text{O} + \text{H}^+ \quad (1)
\]
When plants take up nitrogen in the form of \( \text{NO}_3^- \) ion, the \( \text{NO}_3^- \) ion is first reduced to ammonia, which is subsequently assimilated into amino acids. When \( \text{NO}_3^- \) is reduced in roots, 1 mole of \( \text{OH}^- \) ion is produced for every mole of \( \text{NO}_3^- \) reduced to \( \text{NH}_3 \) \[\text{Eq. (2)}\]. When \( \text{NH}_3 \) is assimilated into amino acids, small amounts of \( \text{H}^+ \) ions are produced through the dissociation of carboxyl groups of amino acids. The resulting negative charge on the carboxylate group can be balanced by the basic cations that entered the root to balance \( \text{NO}_3^- \) uptake. The net excess of \( \text{OH}^- \) ions can either be excreted into the rooting media \[33,35,51\] or neutralized by the malate pH stat \[24,26\]. When \( \text{NO}_3^- \) is reduced in the shoot in order to maintain pH balance in the shoot, the \( \text{OH}^- \) ions released must be neutralized by the malate pH stat described earlier. Unlike the root, the shoot has no external medium in which to excrete the net \( \text{OH}^- \) ions produced in the process of \( \text{NO}_3^- \) assimilation. Malate or another organic anion (e.g., oxalate), along with the cation, is either stored in the vacuole of shoot cells or moves to roots, where decarboxylation of malate in the roots releases \( \text{CO}_2 \) and \( \text{OH}^- \) ions, both of which can be excreted into the nutrient medium.

Thus, if \( \text{NO}_3^- \) is entirely assimilated in roots, the amount of \( \text{OH}^- \) ions produced is often close to 1 mole per mole \( \text{NO}_3^- \) taken up. If \( \text{NO}_3^- \) is assimilated in shoots, however, depending upon the storage capacity of the shoot for products of malate decarboxylation, the amount of \( \text{OH}^- \) ions released ranges from 0 to 1 mole per mole of \( \text{NO}_3^- \) taken up.

\[
\text{NO}_3^- + 8\text{H}^+ + 8e^- \rightarrow \text{NH}_3 + 2\text{H}_2\text{O} + \text{OH}^- \quad \text{(2)}
\]

### 2.1.3 Uptake and Assimilation of Sulfur

Sulfate (\( \text{SO}_4^{2-} \)) is assimilated into sulfur-containing amino acids (cysteine, cystine, and methionine) in the form of sulfhydryl (—\( \text{SH} \)) groups. This reduction process is similar to \( \text{NO}_3^- \) assimilation and produces 2 net moles of \( \text{OH}^- \) for each mole of sulfate assimilated \[\text{Eq. (3)}\] \[36\]. On decomposition of sulfhydryl-containing amino acids, two \( \text{H}^+ \) ions are generated for each mole of —\( \text{SH} \) oxidized to sulfate. Because plants require 10 times less \( S \) than \( N \) (e.g., 4 g S kg\(^{-1}\) vs. 40 g N kg\(^{-1}\)), assimilation of \( \text{SO}_4^{2-} \) has only a small effect on proton balance in plants, and likewise decomposition of \( S \)-containing proteins contributes little to acid generation in soils.

\[
\text{SO}_4^{2-} + 8\text{H}^+ + 8e^- \rightarrow \text{SH}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad \text{(3)}
\]

### 2.2 Soil-Induced Processes

#### 2.2.1 Decomposition of Organic Matter

As microorganisms decompose and respire soil organic matter, they release \( \text{CO}_2 \) \[\text{Eq. (4)}\]. The concentration of \( \text{CO}_2 \) in the soil air is normally between 0.15 and 0.65% (v/v) \[52\], and the pKa for the reaction is around 6.1.

\[
\text{Organic carbon (C)} + \text{O}_2 \rightarrow \text{CO}_2 \quad \text{(4)}
\]
CO₂ dissolves in water to form carbonic acid (H₂CO₃). Carbonic acid in the soil dissociates to form H⁺ ions [Eq. (5)]:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-
\] (5)

The continuous production of CO₂ through soil and root respiration drives this reaction to the right. The concentration of CO₂ in the soil air spaces is usually at least 10 times greater than that in the atmosphere, so the strength of soil acid from this source is considerably greater than that from CO₂ dissolved in rainwater. However, acidic soil solutions of pH 5 hold very little CO₂. Thus, respiration is unlikely to cause soil pH to drop below 5.

Soil microorganisms produce organic acids when they are decomposing plant litter rich in organic compounds but low in the concentrations of organates (RCOO⁻) balanced by basic cations (Eq. 6).

\[
\text{Organic C} \rightarrow \text{RCOOH} \rightarrow \text{RCOO}^- + \text{H}^+
\] (6)

A number of low-molecular-weight organic acids have been isolated from soils [53–55]. Depending upon the nature of the plants growing in a particular soil, different types of plant litter are produced and different amounts of organic acids are generated. The litter layers derived from the great kauri trees in Northland of New Zealand produced large quantities of organic acids; i.e., their litter is not rich in cations. Not only did these litters acidify the soil, but their organic acid decomposition products caused many minerals and plant nutrients to be mobilized and leached from the acidified layer. In general, forest soils that have thick litter layers tend to be more acidic than grassland soils. Further, the litter from conifers tends to produce more organic acids when decomposed than the leaf fall from deciduous woodlands [56].

### 2.2.2 Transformation of Nitrogen

**Ammonification.** Ammonification describes enzymatically catalyzed microbial processes that hydrolyze organic N compounds to yield NH₄⁺ ions. The process includes enzymatic deaminization of amino compounds derived from proteins, amino-polysaccharides, and nucleic acids and enzymatic hydrolysis of urea added through fertilizer application and urine deposition. These two reactions can be expressed as follows [Eqs. (7) and (8)]:

\[
\begin{align*}
\text{R—CH—COOH} + \text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- & \xrightarrow{\text{enzymatic deamination}} \text{R—CH₂—COOH} + \text{NH}_4^+ + \text{OH}^- \\
\text{NH}_2—\text{CO—NH}_2 + 3\text{H}_2\text{O} & \xrightarrow{\text{hydrolysis}} 2\text{NH}_4^+ + 2\text{OH}^- + \text{CO}_2
\end{align*}
\] (7, 8)

The ammonification process results in the consumption of H⁺ ions (or release of OH⁻ ions). This is the main reason why soon after urea application or urine deposition, the pH around the urea granule and the urine spot increases to al
kaline conditions (around pH 7.5 to 8.0). The alkaline pH conditions induce the conversion of \( \text{NH}_4^+ \) ions to \( \text{NH}_3 \) gas, leading to the volatilization loss of ammonia. However, subsequent conversion of \( \text{NH}_4^+ \) ions to \( \text{NO}_3^- \) ions results in the release of \( \text{H}^+ \) ions, leading to soil acidification (see later).

**Nitrification.** The process whereby \( \text{NH}_4^+ \) is oxidized to yield \( \text{NO}_3^- \) ions is referred to as nitrification. Simplistically, the process can be considered in two steps: oxidation of \( \text{NH}_4^+ \) to \( \text{NO}_2^- \) and subsequent oxidation of \( \text{NO}_2^- \) to \( \text{NO}_3^- \). The overall reaction can be expressed as follows [Eq. (9)]:

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \tag{9}
\]

Both heterotrophic and autotrophic microorganisms are involved in the oxidation of \( \text{NH}_4^+ \) to \( \text{NO}_3^- \). Groups of autotrophic bacteria, *Nitrosomonas* and *Nitrobacter*, have been considered the most important nitrifying microorganisms in many agricultural soils, but the importance of their role in pasture soils is not clear.

Whereas the ammonification process results in the release of \( \text{OH}^- \) ions, the nitrification results in the release of \( \text{H}^+ \) ions. Combined ammonification [Eq. (8)] and nitrification [Eq. (9)] of organic N compounds, including urea, in theory generate one net mole of \( \text{H}^+ \) for every mole of N transformed. Oxidation of ammoniacal fertilizers can generate two net moles of \( \text{H}^+ \) for every mole of N. This is consistent with the observation made by many workers that the extent of soil acidification was generally higher with ammoniacal than with urea fertilizers. Addition of basic nitrate fertilizers such as Ca(NO\(_3\))\(_2\) and NaNO\(_3\), however, causes little change or sometimes increases the soil pH [14,15,22,23,57–60].

**Denitrification.** Denitrification is defined as the microbial reduction of \( \text{NO}_3^- \) to gaseous N either as molecular \( \text{N}_2 \) or as an oxide of N under anaerobic conditions. The reactions involved can be simplified as follows [Eq. (10)]:

\[
2\text{NO}_3^- + 2\text{H}^+ \rightarrow \text{N}_2 + 2.5 \text{O}_2 + \text{H}_2\text{O} \tag{10}
\]

Denitrification can also occur from incomplete nitrification in the presence of high \( \text{NH}_4^+ \) concentrations and low oxygen supply [Eq. (11)].

\[
2\text{NH}_4^+ + 2\text{O}_2 \rightarrow 2\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} \tag{11}
\]

The denitrification reactions that consume \( \text{H}^+ \) ions are essentially the reverse of those for nitrification in which \( \text{H}^+ \) ions are produced [Eq. (9)]. Thus, the amount of acidity entering and remaining in the soil from ammoniacal N sources depends largely on the relative magnitudes of the nitrification and denitrification processes [61]. One mole of \( \text{H}^+ \) ions is consumed per mole of \( \text{NO}_3^- \) or \( \text{NO}_2^- \) reduced to \( \text{N}_2 \). The combined sequence of organic N decomposition involving ammonification and nitrification followed by denitrification creates no net proton gain.
Ammonia Volatilization. Ammonium ions in an alkaline medium dissociate into gaseous ammonia, which is subject to volatilization loss [62] [Eq. (12)]. During NH₃ volatilization, the pH of the soil decreases due to the consumption of OH⁻ ions (or release of H⁺ ions) as NH₄⁺ is converted to NH₃. Ammonia volatilization occurs when the soil pH is high (>7.5). In the case of urea nitrogen, the initial increase in soil pH through the ammonification process is likely to result in ammonia volatilization.

\[
\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} \quad \text{(pK}_a 7.6) \tag{12}
\]

2.2.3 Transformation of Sulfur

In aerobic soils, a large proportion of S is present in organic form in recent litter and roots and more humified organic matter. Sulfur in soil organic matter and plant litter is mainly present as sulfhydryl (—SH) groups in proteins, nucleic acids, and sulfolipids and bonded directly to C. Protons are produced during the mineralization and subsequent oxidation of S in soil organic matter [Eq. (13)].

\[
\text{Organic S} + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \tag{13}
\]

As soil bacteria and fungi grow on plant litter and soil organic matter rich in C and poor in S, soil solution SO₄²⁻ may be immobilized. In this case, Eq. (13) is reversed and becomes a proton-consuming reaction as SO₄²⁻ is assimilated to microbial protein.

In periodic anaerobic conditions that occur following aerobic generation of SO₄²⁻, the oxygen concentration may be depleted by rapidly growing bacteria. Some bacteria have the capacity to use SO₄²⁻ as a terminal electron acceptor for fermentation. The result is proton consumption as SO₄²⁻ is reduced along a chain of intermediate compounds to H₂S. It is common for H₂S to react with metal ions to precipitate as metal sulfides. This process is a proton-consuming process. However, when these metal sulfides are reoxidized, they generate protons and acidify the soil. This sequence of reactions is common in soils used for lowland rice cultivation and results in a phytophilic neutral pH when waterlogged but can create low phytotoxic pH when the soil is in the aerobic state.

Elemental sulfur (S°) is frequently used as the ultimate high analysis S fertilizer or in a finely divided form as a fungicide. When elemental sulfur is added to soils, it is oxidized to sulfuric acid that dissociates into SO₄²⁻ and H⁺ ions [Eq. (14)].

\[
2\text{S}° + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+ \tag{14}
\]

In some soils, a portion of the acidity is neutralized by the OH⁻ ions released during the ligand-exchange adsorption of SO₄²⁻. Increases in soil pH due to the ligand-exchange adsorption of SO₄²⁻ have often been observed in soils rich in variable charge components, such as iron and aluminum oxides [20]. This process
is commonly referred to as a “self-liming effect” [63]. The self-liming effect is based on the adsorbed \( \text{SO}_4^{2-} \) displacing \( \text{OH}^- \) from hydrous iron and aluminum oxide surfaces, followed by hydrolysis and precipitation of exchangeable aluminum as aluminum hydroxide.

### 3 NUTRIENT CYCLING PROCESSES THAT LEAVE SOIL ACIDIC

#### 3.1 Uncoupling of Nutrient Cycles

In a closed system, where C, N, and S cycling processes are in steady state and there is no net gain or loss of nutrients, no net generation of \( \text{H}^+ \) ions occurs by nutrient transformations. For nitrogen, this point has been clearly presented by Hel- yar [64], Van Breeman et al. [65], and Breeuwsma and De Vries [66]. The net \( \text{H}^+ \) ions generated by ammonification and nitrification of \( \text{R—NH}_2 \) to \( \text{NO}_3^- \) are subsequently neutralized when \( \text{H}^+ \) ions are consumed during the reduction of \( \text{NO}_3^- \) and synthesis of \( \text{R—NH}_2 \) in the plant (processes 1 and 3 in Fig. 1). However, these two \( \text{H}^+ \) ion-balancing processes are spatially compartmentalized between the soil and the plant and are linked through the plant uptake of highly mobile \( \text{NO}_3^- \) and the return of organic N to the soil as plant residue or animal excreta. Changes in the amounts of these forms of N and/or their loss from the cycle therefore uncouples the \( \text{H}^+ \) balance and leads to permanent soil acidification.

To improve the productivity of soils to economic levels, the plant-available pool of N is increased either by stimulating biological fixation of \( \text{N}_2 \) in situ or by the application of N fertilizers or manures. As N input increases, it is likely that accumulation of soil organic N, removal of organic N products, and leaching of increasing quantities of \( \text{NO}_3^- \) occur. Depending upon the form of N inputs into the farming system, each of these changes will induce an increase in soil acidity.

#### 3.2 Accumulation of Soil Organic Matter

The following two scenarios can be presented in which the accumulation of soil, plant, and animal organic N will result in permanent soil acidification:

1. When uptake and assimilation of \( \text{NH}_4^+ \) or \( \text{N}_2 \) occur in plants, \( \text{H}^+ \) ions are excreted into the rhizosphere soil. If soil organic N or litter N in a forest ecosystem accumulates, the \( \text{OH}^- \) ion generating processes (ammonification and decarboxylation of organic acid anions) are uncoupled from the \( \text{H}^+ \) ion generating processes in the rhizosphere. As more organic N accumulates in the rhizosphere, acidity should increase, eventually affecting bulk soil pH [5,67–69].

2. When fertilizer \( \text{NH}_4^+ \) is nitrified, two net \( \text{H}^+ \) ions are generated per N atom. These \( \text{H}^+ \) ions can be neutralized only if all the \( \text{NO}_3^- \) produced is
taken up and assimilated into plant organic N (one OH\(^-\) is either extruded into the rhizosphere or stored as organic anion in the plant) and the plant organic N (or breakdown products, e.g., animal excreta) is subsequently ammonified and the organic anion decarboxylated upon decomposition of the plant [70]. Thus, only if all N returns to the input form (NH\(_4^+\)) will there be neutrality. If organic N accumulates, the NH\(_4^+\)-fertilized system can generate an excess of one H\(^+\) per atom of N accumulated.

Similarly, if instead of accumulating, plant or animal products are removed, nonneutralized H\(^+\) ions remain in the soil. This may also include the uneven transfer of animal excreta within one paddock or loss of excreta to unproductive areas of the farm, such as raceways and yards. Losses of N through NH\(_3\) volatilization or denitrification produce permanent soil acidity only when the N input is added in NH\(_4^+\) form through ammoniacal fertilizer and ammonium-rich wastewaters, such as dairy and piggery effluents.

### 3.3 Leaching of Nutrients

In most soils, NO\(_3^-\) is more readily leached than SO\(_4^{2-}\). Nitrate leaching induces permanent soil acidity only when the loss of NO\(_3^-\) uncouples an H\(^+\) ion-balancing system. The following two scenarios can be presented in which the uncoupling of NO\(_3^-\) leaching and an H\(^+\) ion-balancing system will lead to permanent acidification:

1. If NH\(_4^+\) or R—NH\(_2\)—based fertilizers are added and are subsequently oxidized to NO\(_3^-\) in the soil, two (nitrification) and one (ammonification + nitrification) net H\(^+\) ions are generated, respectively. These H\(^+\) ions can be neutralized only if the NO\(_3^-\) is completely transformed by the N cycle back into the original input forms. If NO\(_3^-\) is lost from the system, the H\(^+\) remains as permanent soil acidity [64].

2. If we consider N transformations only, uptake and assimilation of N\(_2\) into plant protein constitute a proton-neutral process. During the decomposition of the plant protein, through various breakdown products (e.g., urea in animal excreta) to NH\(_4^+\) and then via nitrification to NO\(_3^-\), 1 mole of H\(^+\) ions is generated per mole of N transformed. Unless all the NO\(_3^-\) is reassimilated by plants or microorganisms into protein, the excess H\(^+\) ions from the nitrification of R—NH\(_2\) will remain in the soil.

In both of the preceding cases, the surplus H\(^+\) ions will remain in the soil when cations other than the H\(^+\) ions are leached as companion ions with the negatively charged NO\(_3^-\) ions [40,61]. It is the mobile exchangeable basic cations, Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), and Na\(^+\), that are usually leached in exchange for H\(^+\). As soil acidity accumulates, the concentration of basic cations in soil decreases, resulting
in the leaching of H⁺ ions as the companion cation. Thus, in very acid soils, NO₃⁻ leaching may induce less H⁺ accumulation than in soils high in exchangeable basic cations. In extreme cases, leaching of H⁺ ions with NO₃⁻ could be a cause of subsoil and ground water acidification (for further discussion see Chapter 3).

3.4 Fertilizer Reactions

As discussed earlier, application of N fertilizers, such as urea and ammonium sulfate, to soils can produce H⁺ ions through oxidation of NH₄⁺ ions to NO₃⁻ ions (nitrification). Because the NO₃⁻ ions are not strongly adsorbed by the soil, it is common that some of the NO₃⁻ ions not taken up by the crop are liable to leach or move down through the soil. The negatively charged NO₃⁻ ions are accompanied by positively charged basic cations, such as Ca²⁺, Mg²⁺, K⁺, and Na⁺, in order to maintain the electric charge on the soil particles. It is the exchange of these ions on cation exchange sites for H⁺ and the loss of NO₃⁻ ions that can potentially generate OH⁻ ions (during plant uptake) and accelerate the acidification process.

The amount of acid produced by N fertilizers depends on the amount of NO₃⁻ removed by plant uptake and leaching. It is estimated that approximately 1.72 and 5.24 kg of lime are required to overcome the acidity produced by the application of 1 kg of N as urea and ammonium sulfate, respectively. Therefore, if N is added as urea (46% N) at a rate of 25 kg N per ha, then 43 kg lime per ha is needed to neutralize the acidity produced.

In legume-based pastures, phosphate fertilizers produce acids by two processes, namely (1) fertilizer reaction with the soil and (2) in P-deficient soils, stimulation of legume growth and nitrogen fixation. Dissolution of superphosphate fertilizers (mostly monocalcium phosphate) in soils results in the production of di-calcium phosphate and phosphoric acid close to the fertilizer granules [Eq. (15)]. The phosphoric acid dissociates to phosphate and H⁺ ions. A fraction of the H⁺ ions produced is neutralized by OH⁻ ions released during the ligand-exchange adsorption of phosphate ions by soil components. It is estimated that at an annual application rate of 400 kg single superphosphate (10% P) per hectare, approximately 32 kg lime is required to neutralize the acid produced directly by fertilizer dissolution.

\[
\text{Ca(H}_2\text{PO}_4\text{)}_2 \rightarrow \text{CaHPO}_4 + \text{H}_3\text{PO}_4 \rightarrow 2\text{H}_2\text{PO}_4^- + \text{H}^+ \quad (15)
\]

When elemental sulfur is added to soils, it is oxidized to sulfuric acid that dissociates into SO₄²⁻ and H⁺ ions [Eq. (14)]. It is estimated that a maximum of approximately 3.1 kg of lime is required to neutralize H⁺ produced from the oxidation of 1 kg of elemental sulfur. In both cases of adding P and S fertilizers to legume-based pastures, the extra N input and cycling from the fertilizer-responsive legume result in greater soil acidification than that caused directly by fertilizer reactions with soils.
4 A SYSTEM CASE STUDY—ACIDIFICATION IN
LEGUME-BASED PASTURES

Virtually all New Zealand’s and Australia’s animal-based exports are produced
through the management of legume-based pastures. On many productive lowland
pastures, liming to overcome continuing soil acidification has become a regular
management practice required to maintain pasture production and animal health

The current method for estimating lime requirements in pasture soils in New
Zealand [71] is based on the relationship between soil pH and response to lime.
This method has major limitations mainly because this relationship is rather poor
[72] and is derived empirically rather than from knowledge of the underlying
mechanisms of soil acidification [12]. The incorporation of a mechanistic model
for predicting soil acidification rates into the current lime requirement model is
expected to improve the accuracy of this approach. Furthermore, in situations
where the optimal soil pH is known, a soil acidification model can be used to cal-
culate the amount of lime required for maintaining the soil pH at the desired level.
In addition, in areas where liming is thought to be uneconomic (e.g., hill and high
country farming in New Zealand and areas remote from liming sources in Aus-
tralia) because of high application costs, a predictive soil acidification model is
useful in defining pasture sustainability for these areas.

A number of models have been developed to predict soil acidification that
incorporate the mechanisms of various processes responsible for soil acidification
[1,2,12,72]. These models are discussed in detail elsewhere in this book (see
the net input of H\(^+\) ions into a system from processes involving the various nutri-
tent cycles that occur in the soil. Sinclair [72] considered NO\(_3\) leaching and nutri-
tent transfer as the two main causes of soil acidification and presented a model for
estimating the animal-induced acidification based on stocking rate. These models
require quantitative information on the processes responsible for soil acidifica-
tion. De Klein et al. [12] extended the model developed by Sinclair [72] to incor-
porate submodels for estimating the extent of NO\(_3\) leaching, nutrient transfer or
removal, and soil organic matter accumulation.

In this section we illustrate the concept of predicting the rate of acidification
and future lime requirement of a soil from knowledge of the gains and losses of C,
N, and S from the production system. The simplest system to consider and perhaps
the most appropriate to New Zealand and Australia grassland is the one in which
all N has entered the “improved” pasture as symbiotically fixed N\(_2\) [2].

4.1 Acidification of the Rhizosphere

The mechanisms generating H\(^+\) ions in the legume rhizosphere were discussed in
previous sections. The acidity generated by the assimilation of CO\(_2\) and N\(_2\) in
legumes is equivalent to the uptake of excess inorganic cations over anions by the legume. This assumes that N₂ assimilation into protein is a proton-neutral process. Nyatsanga and Pierre [37] have shown it is reasonable to assume that the amount of net excess cations per unit of plant-N is relatively constant for legume crops. Thus, for a standing legume crop, the number of H⁺ ions generated in the rhizosphere soil \( R_L H^+ \) mol H⁺ ha⁻¹ can be estimated from the excess cation/nitrogen ratio and the total amount of N accumulated [Eq. (16)].

\[
R_L H^+ = N_a \left( \frac{\sum C_L - \sum A_L}{N_c} \right)
\]  

(16)

where

\( N_a = \) total amount of biologically fixed N accumulated in the standing legume (kg N ha⁻¹)

\( \sum C_L = \) sum of inorganic cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) in the legume (mol charge kg⁻¹ DM)

\( \sum A_L = \) sum of inorganic anions (SO₄²⁻, H₂PO₄⁻, Cl⁻) in the legume (mol charge kg⁻¹ DM)

\( N_c = \) concentration of legume N (kg N kg⁻¹ DM).

When N enters the sward only through N₂ fixation, even if the sward contains grasses that take up NO₃⁻ or NH₄⁺ derived from the decomposition of the clover, it can be shown that rhizosphere acidity can be calculated from the excess cationic charge in a mixed sward sample and the accumulated amount of organic N. All N transfers from N₂ to R—NH₂ in the grass have charge balance and cause no net change in pH. Net rhizosphere H⁺ arises solely from the synthesis and dissociation of organic acids within the plant. For mixed clover–ryegrass swards at seven sites in the lower North Island of New Zealand, the excess cation/nitrogen ratio in the clover plant approximating 0.4:1, was found to be very similar to that in ryegrass [73]. This ratio is similar to that obtained for alfalfa (0.41:1) [37] and for soybean (0.36:1) [41].

4.2 Acidification Due to Organic Matter Accumulation and Product Removal

The H⁺ ions exported from mixed sward roots in exchange for the accumulation of anionic charge will remain in the rhizosphere soil if the organic anions synthesized by the plant and their associated basic cations either accumulate in organic matter within the pasture system or are removed from the site of N₂ and CO₂ assimilation. Such removal occurs with the removal of animal products and excreta from a legume-based grazing system. In such a system the acidity generated in the rhizosphere soil of the sward could be estimated from Eq. (17).

\[
\sum C_L - \sum A_L = N_a
\]
Permanent acidity in the sward ($R_{sH^+}$) in mol $H^+$ ha$^{-1}$ is given by

$$R_{sH^+} = (\Delta SN + XN) \left( \frac{\Sigma C_s - \Sigma A_s}{N_c} \right)$$  \hspace{1cm} (17)

where $\Delta SN$ is the increase in soil, plant, or animal N (kg ha$^{-1}$), $XN$ is the amount of N exported in animal products and excreta (kg ha$^{-1}$), and $\Sigma C_s$, $\Sigma A_s$, and $N_c$ for the sward are as defined in Eq. (16) but for practical purposes could be measured as the mean annual sums of accumulated cations and anions and N concentration of the sward. This approximation assumes that the ratio of excess moles of anionic charge to moles of N in the accumulated organic matter and the organic products that were removed is similar to that in the mixed sward. A more accurate method would be to measure the excess of inorganic cations over anions in the materials removed [1].

### 4.3 Acidification Through Nutrient Leaching

For every NO$_3^-$ ion leached in the drainage water, one $H^+$ ion remains at the site of nitrification. This occurs when the cation accompanying the NO$_3^-$ is a basic cation (i.e., other than $H^+$ ion). Thus, in a system where all N input is derived from biological fixation of N$_2$, the $H^+$ ions generated by NO$_3^-$ leaching ($L_{NH^+}$) can be calculated from Eq. (18). This assumes that no significant amount of $H^+$ appears in the drainage water.

$$L_{NH^+} = \Sigma NO_{3L}$$  \hspace{1cm} (18)

where $\Sigma NO_{3L}$ is the cumulative amount of NO$_3^-$ leached (mol charge ha$^{-1}$).

In most soil acidification models [1,74], NO$_3^-$ leaching is calculated from the difference between the total acid production, as assessed from changes in pH and the pH buffering capacity, and the acid addition from processes other than NO$_3^-$ leaching. De Klein et al. [12] developed a mechanistic model to predict soil acidification for pasture system in which they incorporated a submodel to estimate NO$_3^-$ leaching.

### 4.4 Predicting Acidification

For working examples of farms mostly dependent upon biological N$_2$ fixation, we take the examples of the farms given in Table 3 [75]. As no detailed data on drainage water composition are available, Eq. (18) is used to estimate the permanent acidity generated from NO$_3^-$ leaching. Combining Eqs. (17) and (18) gives

$$R_{sH^+} + L_{NH^+} = \left[ (\Delta SN + XN) \left( \frac{\Sigma C_s - \Sigma A_s}{N_c} \right) \right] + \Sigma NO_{3L}$$  \hspace{1cm} (19)
The increases in soil, plant, and animal N (ΔSN), the amount of N exported from the system (XN), and the amount of N leached (ΣNO3L) are given in Table 3. The amount of excess cationic charge per mole of N taken up by plants ((ΣCs - ΣAs)/Nc) was derived from the data of Metson and Saunders [73]. The amount of H⁺ ions generated from excess cation uptake (RSH⁺) and from NO3 leaching (LNH⁺) and the amounts of lime (CaCO3) required to neutralize this excess acidity were calculated (Table 4).

Table 4 shows that the net amount of H⁺ ions generated in the first two farms in New Zealand is much higher than that in the third farm in Australia. This is due to the higher amounts of N cycled, accumulated, and leached in the former farms than in the latter. A number of studies have shown that higher levels H⁺ ions are produced in New Zealand than in Australia (Table 1).

In the first two New Zealand farms, the predicted amounts of H⁺ ions generated were higher than those inferred from the annual lime requirement [11] (Table 4). Such an overestimate, based on comparing predicted soil H⁺ ion gen-
eration with changes in surface soil pH, might be accounted for by macropore flow of urine that bypassed the surface soil. Nitrification of some urea would take place at depth and would result in one net H$^+$ ion per atom of N remaining in the subsoil. Nitrate would still appear in the drainage water, but as urea had bypassed the topsoil, topsoil pH would remain unchanged. Williams et al. [76] estimated that for a Yellow brown loam soil similar to the one at Waikato, approximately 15% of all urine N could be lost from the topsoil by macropore flow of urine. On the Waikato farm [77] this would amount to 44 kg N ha$^{-1}$ year$^{-1}$, which is 37% of the entire N appearing in the drainage. If this is taken into account, the net amount of H$^+$ ion produced would be 7.7 kmol H$^+$ ha$^{-1}$ year$^{-1}$, equivalent to a lime requirement of 385 kg year$^{-1}$, which is very close to the rate recommended by Pringle et al. [11].

The estimated amount of H$^+$ ions generated in the third farm in Australia (1.08 kmol H$^+$ ha$^{-1}$ year$^{-1}$) may be compared with an increase of approximately 1.1 and 0.8 kmol H$^+$ ha$^{-1}$ year$^{-1}$ in exchange acidity of Coolup sandy soils [78] and the Yellow podzolic soils [5] under subterranean clover pastures in Western Australia and New South Wales, respectively. There is, however, a huge variation in the rate of acidification as shown in Table 1. The extent of soil acidification, as measured by a decrease in soil pH, depends mainly on the pH buffering capacity of the soil. Various soil constituents such as organic matter, Fe and Al oxides, and CaCO$_3$ (in calcareous soil) contribute to pH buffering of soils at different pH values [79–81]. In many Yellow brown loams and Yellow gray earth soils in New Zealand and Xanthozems and podzolic soils in Australia, the rates of soil acidification calculated in the preceding examples may remain unnoticed for several years because these soils can have short-term pH buffering capacities of approximately 90 and 30 kmol ha$^{-1}$ for a unit change in pH, respectively [82]. Thus, in the case of the first two farms where the annual net H$^+$ ion input into the surface soil is on the order of 1 kmol ha$^{-1}$ it may take 30 years to cause a unit drop in soil pH. It has been observed that continuous pasture of subterranean clover in Aus-

### Table 4  The Amount of Protons Generated in the Case Study Farms

<table>
<thead>
<tr>
<th>Farm</th>
<th>Fixed N (kg ha$^{-1}$ year$^{-1}$)</th>
<th>$\Delta$SN</th>
<th>XN</th>
<th>$\Sigma$ NO$_3$L</th>
<th>RsH (kmol H$^+$ ha$^{-1}$ year$^{-1}$)</th>
<th>$L_{SN}$H$^+$</th>
<th>Total H$^+$ (kmol H$^+$ ha$^{-1}$ year$^{-1}$)</th>
<th>CaCO$_3$ requirements (kg ha$^{-1}$ year$^{-1}$)</th>
<th>Predicted</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waikato</td>
<td>267 (94)$^b$</td>
<td>8</td>
<td>112</td>
<td>110</td>
<td>3.51</td>
<td>7.85</td>
<td>11.36</td>
<td>550</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>Canterbury</td>
<td>180 (20)</td>
<td>20</td>
<td>30</td>
<td>100</td>
<td>1.46</td>
<td>7.14</td>
<td>8.60</td>
<td>430</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>Townsvile</td>
<td>43 (91)</td>
<td>37</td>
<td>0</td>
<td>—</td>
<td>1.08</td>
<td>—</td>
<td>1.80</td>
<td>54</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Value of (\(\Sigma\ C_k - \Sigma\ A_k\))/Nc is taken as 0.41.

$^b$ Values within parentheses in column two represent the percentage contribution of fixed N to the total N in the system, the rest coming from rainfall.
Australia has resulted in a decrease in soil pH at a rate of 0.018 to 0.036 pH unit per year, indicating that it takes approximately 27 to 53 years to cause a change of one pH unit [5,6,78,83]. Furthermore, in the longer term these soils are expected to have even greater pH buffering in regions close to pH 5.

5 MINIMIZING SOIL ACIDIFICATION

Acidification of soils under managed ecosystems occurs mainly through uncoupling of the processes generating $\text{H}^+$ and $\text{OH}^-$ in the C, N, and S cycles. To minimize the rate of acidification and the negative impacts on agricultural production, three approaches can be taken: (1) reduce the amount of $\text{H}^+$ ions generated, (2) reduce the uncoupling of processes generating $\text{H}^+$ and $\text{OH}^-$ ions, and (3) neutralize the acid produced. The rate of acid generation can be altered by selecting the nutrient forms added to soil–plant systems that produce less acid and selecting plant species that do not accumulate cation excesses. Permanent soil acidification can be minimized mainly by reducing the loss of C, N, and S from the system to drainage, product losses, or noncycling pools (e.g., soil organic matter accumulation).

Liming is most commonly practiced to overcome the impact of soil acidification. However, an integrated approach involving liming, management practices, and plant tolerance will probably be necessary, particularly where the acidification potential is high and acidification is likely to extend into the subsoil. Cregan et al. [84] and Helyar [85] identified a number of management practices to minimize soil acidification. These include using less acidifying fertilizers, improving nutrient use efficiency, reducing nutrient leaching losses, and reducing product removal.

5.1 Use of Less Acidifying Fertilizers

Fertilizers vary in their rates of soil acidification. The acidifying effect of fertilizer materials is expressed as acidity equivalent. The *acidity equivalent* is defined as the number of parts of pure lime (calcium carbonate) required to neutralize the acidity caused by 100 parts of a fertilizer material (Table 5). The acidity equivalents reported are only approximate “rule of thumb” values, and the amount of acidity generated is dependent upon the fate of the fertilizer N, P, or S in the system. The number of years required to reduce the pH by one unit by these fertilizers for two soils that vary in their pH buffering capacities are also presented (Table 5). The data indicate that ammonium-based fertilizers produce greater amounts of acidity than the urea- and nitrate-based fertilizers. Nitrate, sulfate, and phosphate rock fertilizers have negative acidity equivalents, indicating that these fertilizers provide some liming value. A number of workers have compared the acidifying effects of various fertilizers under both laboratory [58,86] and field conditions [15,23,59,60] and observed that ammonium-based fertilizers have the highest
Choosing a fertilizer with a low or negative acidity equivalent (Table 5) can help to minimize soil acidification.

### 5.2 Improving Nutrient Use Efficiency

The nutrient use efficiency of plants can be improved through the use of slow-release fertilizers, split application of fertilizers, placement in the root zone, and selection of deep-rooted plant species. Wang and Alva [87] observed that slow-release N fertilizers (isobutylidene diurea and polyolefin resin–coated urea) reduced the leaching losses compared with readily soluble N fertilizers and thereby increased the N utilization by plants. Split application of fertilizers has often increased the nutrient utilization by plants [88]. Perennial pasture species can reduce water losses from deep drainage compared with annual species [89], thereby decreasing the leaching losses of mobile nutrients such as nitrate. Ridley et al. [74] observed higher soil pH values under a *Phalaris*-based pasture than under a comparable annual grass and subterranean clover–based pasture; the net acid addition to soil was calculated to be 0.7 kmol H⁺ ha⁻¹ year⁻¹ less under the *Phalaris* pasture. A decrease in NO₃⁻ leaching under these species is considered to be the main

---

**TABLE 5** Acidifying Effects of Various Fertilizers

<table>
<thead>
<tr>
<th>Fertilizers</th>
<th>Acidity equivalentᵃ</th>
<th>Acidity produced (kmol H⁺ ha⁻¹)ᵇ</th>
<th>Number of years required to reduce the pH by one unitᶜ</th>
<th>Tokomaru</th>
<th>Egmont</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>110</td>
<td>2.60</td>
<td>8</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Diammonium phosphate</td>
<td>74</td>
<td>2.06</td>
<td>10</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>79</td>
<td>0.86</td>
<td>25</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Calcium nitrate</td>
<td>−50</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Single superphosphate</td>
<td>8</td>
<td>0.48</td>
<td>45</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Triple superphosphate</td>
<td>15</td>
<td>0.50</td>
<td>43</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>North Carolina phosphate rock</td>
<td>−50</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td>−64</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Elemental sulfur</td>
<td>310</td>
<td>1.55</td>
<td>14</td>
<td>43</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ kg calcium carbonate 100 kg⁻¹ fertilizer; negative value indicates liming value.
ᵇ N fertilizer = 25 kg N ha⁻¹ year⁻¹; P fertilizer = 30 kg P ha⁻¹ year⁻¹; and elemental sulfur = 30 kg S ha⁻¹ year⁻¹.
ᶜ pH buffering capacity (kmol H⁺ ha⁻¹) = 21.7 and 67.5 for the Tokomaru and the Egmont soil, respectively.
reason for lower acidification rates, and thus these species have the potential to reduce soil acidification.

5.3 Reducing Nutrient Leaching Losses

In the N cycle, the NO$_3^-$ leaching is considered to be the major factor inducing permanent soil acidification. It has often been found that cultivation increases the leaching losses of NO$_3^-$ by enhancing the ammonification–nitrification process. Meek et al. [21] have shown that NO$_3^-$ leaching is higher under convention tillage than under direct drilling. Evans et al. [90] have observed greater accumulation of NO$_3^-$ under a grain legume (pea) than a cereal (barley) crop, indicating greater generation of H$^+$ ions. The greater NO$_3^-$ concentrations are likely to accelerate NO$_3^-$ leaching, leaving soil acid non-neutralized. Nitrate leaching also enhances the leaching loss of valuable basic nutrient cations. McKenney et al. [91] have shown that the addition of residues with a high C/N ratio increases the immobilization of N and thereby decreases the leaching losses. Soil amendment with cereal straw has often been found to be effective in reducing NO$_3^-$ concentration under grain legume crops, resulting in reduced acidification through reduced NO$_3^-$ leaching. Similarly, the inclusion of cover crop to reduce soil NO$_3^-$ concentrations may potentially delay the leaching of NO$_3^-$ mineralized during a period of fallowing.

5.4 Reducing Product Removal

Removal of plant residues carrying organic anions and excess cations is likely to accelerate soil acidification. Similarly, the accumulation of partially decomposed organic matter in soils causes soil acidification as observed under clover pasture and lupin–cereal rotations in Australia [9,92]. However, short-term incubation experiments have shown that the addition of organic residues with excess cations increases the pH of the soil [93–95]. Accumulation of organic anions is the primary source of the potential alkalinity that causes an increase in soil pH if decomposed by soil microorganisms. The change in soil pH with the addition of organic matter depends on the rate of release or consumption of H$^+$ by the organic matter added to the soils. The degree of consumption or release of H$^+$ by organic matter is dependent on its initial content of anion charge balanced by basic cations relative to undissociated acid groups, the initial soil pH, the dissociation constant (p$K_a$) of the remaining undissociated organic acids, the extent of dissociation of the organic acids when they are released into soil, and finally the extent of decomposition of the organic matter in the soil.

If the soil pH is less than the p$K_a$ value of the organic acid in the organic matter, there will be an increase in soil pH due to the association of H$^+$ ions from the soil with some of the organic anions [92]. Subsequent decomposition of highly reduced organic matter is likely to generate carboxylic acids as oxidation products. This is common during the decomposition of C-rich cereal straw, and some
of these carboxylic acids may dissociate. If organic anions are decomposed (respired or decarboxylated), they generate HCO$_3^-$ or OH$^-$ ions.

6 CONCLUSIONS

The incomplete cycling of C, N, and to a lesser extent S in soils under agricultural management has been identified as a major cause of increasing soil acidity. In particular, accumulation of undecomposed soil organic matter rich in organates, losses of organates in products, and inputs of symbiotically fixed N and ammonium-based fertilizers with consequent nitrate leaching are involved in the accelerated acidification of agricultural soils.

It is possible to determine the lime requirement of agricultural soils knowledge of the form of N and S inputs and the quantity of basic cations removed by plants, accumulated in organic products, or lost as companion ions with leached nitrate. For legume-based systems, a useful approximation of this lime requirement can be calculated from the amount of N lost or accumulated in organic products, the excess cation charge in the crop or sward, and an estimate of the quantity of nitrate leached. Combined with a knowledge of soil pH buffer capacities, such calculations are useful to predict the long-term lime requirements of a farming system. Accurate estimates of the rate of soil organic matter accumulation and the quantities of NO$_3^-$ leached are the main knowledge gaps limiting the accuracy of this approach for predicting short-term lime requirements.

REFERENCES

70. AE Johnston, KWT Goulding, PR Poulton. Soil acidification during more than 100 years under permanent grassland and woodland at Rothamsted. Soil Use Manage 2:3–10, 1986.
Role of Plant Cation/Anion Uptake Ratio in Soil Acidification

Caixan Tang and Zdenko Rengel
The University of Western Australia, Perth, Australia

1 INTRODUCTION

Soil acidification is a slow natural process that occurs during pedogenesis and can be either accelerated or slowed down by farming practices. The causes of soil acidification in agricultural systems have been attributed mainly to an imbalance in the carbon and nitrogen cycles [1,2] (see Chapter 2). The major processes leading to soil acidification include (1) net H⁺ excretion by plant roots due to excess uptake of cations over anions; (2) removal of alkalinity in farm products such as grain, hay, meat, and wool; (3) accumulation of organic anions in the form of soil organic matter; (4) mineralization of organic matter, nitrification of ammonium, and subsequent leaching of nitrate, and (5) input of acidifying substances such as NH₄⁺-based fertilizers.

Topsoil acidity can be effectively ameliorated by liming (see Chapter 11). However, the development of subsoil acidity [3–8] is of particular concern due to the greater cost and difficulty of amelioration.

Plants take up cations and anions from soil solutions to satisfy their requirement for growth. The relative amounts of various ions absorbed from soil solutions by plant roots are determined by the specific plant requirements for these ions and the composition of the soil solution. In most cases, plants take up more
cation/anion ratio in soil acidification, particularly its contribution to the development of subsoil acidification.

2 CATION/ANION BALANCE AND SOIL ACIDIFICATION

2.1 Proton Extrusion and Cation/Anion Balance

There should be no net charge carried across the plasma membrane, except a small charge imbalance caused by the action of the electrogenic $H^+$-adenosine triphosphatase (ATPase) pumps. Therefore, the uptake of a cation must be accompanied by uptake of an anion(s) of equal but opposite charge or by the extrusion of $H^+$ or other cations. The reverse is true for the uptake of an anion. Plants generally extrude net excess $H^+$ when cation uptake exceeds anion uptake and, conversely, extrude net excess of $OH^-/HCO_3^-$ or consume $H^+$ when anion uptake exceeds cation uptake. These phenomena can be experimentally demonstrated by pH changes in nutrient solution [9] as well as in the rhizosphere of the soil-grown plants by monitoring color changes of pH indicators in the agar overlaid on roots [10] or by using pH microelectrodes [11].

The amount of net excess of $H^+$ or $OH^-$ excreted by the root is equivalent to the respective excess cation or anion uptake by the plant [12]. A number of studies [e.g., 9,13–15] have shown close relationships between excess ion uptake and release of $H^+$ or $OH^-$. For example, when nitrate was the only source of nitrogen, pea plants took up more anions than cations by 1.47 mmol plant$^{-1}$ at day 21 and by 4.2 at day 42, leading to net $OH^-$ extrusion of 1.41 and 4.44 mmol plant$^{-1}$, respectively. In contrast, when relying on $N_2$ fixation, the plants took up more cations than anions by 0.28 mmol plant$^{-1}$ at day 21 and by 1.51 at day 42 and simultaneously released 0.33 and 1.58 mmol $H^+$ per plant, respectively [9]. Similarly, when 12 $N_2$-fixing pasture legumes were grown from 40 to 61 days in nutrient solutions, the amounts of net excess $H^+$ extruded by the plant roots correlated well with excess cation uptake ($r^2 = 0.94$) with an $H^+/excess$ cations ratio of 1.06 [14].

Unbalanced uptake rates of cations and anions tend to cause cytoplasmic pH changes as well as charge imbalance in the plant. Excess cation uptake by the root is associated with a pH increase in the cytoplasm of the root cells, whereas excess anion uptake is associated with a decrease in cytosolic pH [16]. Plant cells are able to maintain their cytosolic pH and charge balance within relatively narrow limits through (1) proton exchange across the plasma membrane and tonoplast and (2) the formation and breakdown of carboxylic groups that are involved in the consumption and production of protons [17].
2.2 Measurement of Cation/Anion Balance

There are three methods of measuring cation/anion uptake ratios: (1) measuring depletion of ions in the root medium, (2) determining excess cations in tissues, and (3) measuring ash alkalinity after incinerating plant tissues. The nutrients whose content is used in calculating the cation/anion balance in plant tissues are NH$_4$/$\text{H}^{+}$, K$^+$/$\text{H}^{+}$, Ca$^{2+}$/$\text{H}^{+}$, Mg$^{2+}$/$\text{H}^{+}$, and Na$^+$ (cations) and NO$_3^-$, H$_2$PO$_4^-$, SO$_4^{2-}$, and Cl$^-$ (anions). Other nutrients are present in plant tissues in small amounts and therefore are not included in the calculation. Although soil-grown plants contain appreciable amounts of silicon [18], it is taken up as uncharged hydrated silicic acid (due to its high pK) and hence does not contribute to the charge balance.

2.2.1 Depletion of Ions in Nutrient Solution

This approach involves the sampling of nutrient solution over a period of time and determining the concentration of ions. The amounts of cations and anions taken up by the plant can be calculated from the change of ion concentration in nutrient solution over time. Using this approach in a split-root study, Loss et al. [19] demonstrated that net excess protons were excreted by the roots of *Lupinus angustifolius* (narrow-leafed lupin) where excess cation uptake occurred, and the net excess hydroxyl ions were excreted where more anions than cations were taken up. The amount of net excess H$^+$ or OH$^-$ extruded was close to the charge difference between amounts of cations and anions depleted from the nutrient solution.

The nutrient depletion method is relatively simple and sensitive for macronutrient cations and anions. The measurable depletion of nutrients can be detected within hours and much earlier in some cases (e.g., K$^+$ and nitrate), and pH change (i.e., net excess H$^+$ extrusion) can be measured simultaneously. However, this method may be applicable only to solution culture and is not feasible for long-term studies.

2.2.2 Accumulation of Excess Cations in Plant Tissues

In this method, individual nutrients in plant tissue need to be analyzed. The concentration of excess cations (or excess base, EB) is calculated as the charge difference between non-N cations and non-N anions and expressed as cmol(+) kg$^{-1}$ dry weight of plant tissue. Thus

\[
\text{Excess cations} = (K^+ + Ca^{2+}_{0.5} + Mg^{2+}_{0.5} + Na^+) - (H_2PO_4^- + SO_4^{2-}_{0.5} + Cl^-)
\]

Because excess cations in plant cells are balanced by organic anions, the measurement of excess cations also provides an estimate of the organic anion concentration in the plant. To estimate cation/anion uptake ratios, the uptake of NH$_4^+$ and NO$_3^-$ needs to be included.

Plant species differ substantially in concentration of excess cations in their tissues, ranging from 25 to 255 cmol(+) kg$^{-1}$ in shoots (Table 1). The concentra-
## Table 1  
### Acid Production and Shoot Excess Cations or Ash Alkalinity (Excess Bases, EB) of N₂-Fixing Legume Species and Selected Cereal Crops

<table>
<thead>
<tr>
<th>Species</th>
<th>Acid production (cmol kg⁻¹ shoot)</th>
<th>EB (cmol kg⁻¹)</th>
<th>Growth conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grain legumes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Cicer arietinum</em></td>
<td>58</td>
<td>108</td>
<td>Soil, 42 d</td>
<td>20</td>
</tr>
<tr>
<td>(chickpea)</td>
<td>44–115</td>
<td>110–144</td>
<td>Soil, various P, 60–64 d</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>143</td>
<td>177</td>
<td>Field, maturity</td>
<td>21</td>
</tr>
<tr>
<td><em>Glycine max</em></td>
<td>72–117</td>
<td>85–104</td>
<td>Soil, 67–73 d</td>
<td>13</td>
</tr>
<tr>
<td>(soybean)</td>
<td>109, 101</td>
<td>102–142</td>
<td>Perlite+solution, 41–151 d</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>106–143</td>
<td></td>
<td>Field survey, flowering stage</td>
<td>25</td>
</tr>
<tr>
<td><em>Lathyrus sativus</em></td>
<td>33</td>
<td>74</td>
<td>Soil, 42 d</td>
<td>20</td>
</tr>
<tr>
<td>(grasspea)</td>
<td>144</td>
<td>122</td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td><em>Lens culinaris</em></td>
<td>132</td>
<td></td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td>(lentil)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Lupinus albus</em></td>
<td>23–43</td>
<td>46–84</td>
<td>Soil, various P, 60–64 d</td>
<td>15</td>
</tr>
<tr>
<td>(white lupin)</td>
<td>93–101</td>
<td>96–142</td>
<td>Soil, 105 and 82 d</td>
<td>13</td>
</tr>
<tr>
<td><em>Lupinus angustifolius</em></td>
<td>19–74</td>
<td>64–113</td>
<td>Soil, various P, 60–64 d</td>
<td>15</td>
</tr>
<tr>
<td>(narrow-leafed lupin)</td>
<td>93, 101</td>
<td>132</td>
<td>Field, maturity</td>
<td>21</td>
</tr>
<tr>
<td><em>Lupinus pilosus</em></td>
<td>178</td>
<td>167</td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td>(rough-seeded lupin)</td>
<td>144</td>
<td>139</td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td><em>Lupinus luteus</em></td>
<td>31–57</td>
<td>57</td>
<td>Field, maturity</td>
<td>21</td>
</tr>
<tr>
<td>(yellow lupin)</td>
<td>82–107</td>
<td></td>
<td>Soil, various P, 60–64 d</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>96</td>
<td>Soil, 42 d</td>
<td>20</td>
</tr>
<tr>
<td><em>Pisum sativum</em></td>
<td>27–31</td>
<td>64–68</td>
<td>Soil, 42 d</td>
<td>20</td>
</tr>
<tr>
<td>(field pea)</td>
<td>78–115</td>
<td>110</td>
<td>Solution, 42 d</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>112</td>
<td></td>
<td>Field</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>116</td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>132, 120</td>
<td>112, 115</td>
<td>Solution, 21 and 42 d</td>
<td>9</td>
</tr>
</tbody>
</table>

(continues)
### TABLE 1  Continued.

<table>
<thead>
<tr>
<th>Species</th>
<th>Acid production (cmol kg(^{-1}) shoot)</th>
<th>EB (cmol kg(^{-1}))</th>
<th>Growth conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Vicia faba</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(faba bean)</td>
<td>34</td>
<td>77</td>
<td>Soil, 42 d</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>32–68</td>
<td>60–122</td>
<td>Soil, various P,</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60–64 d</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Field, maturity</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>145</td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td><em>Vicia sativa</em></td>
<td>149</td>
<td>126</td>
<td>Solution, 42–49 d</td>
<td>13</td>
</tr>
<tr>
<td>(common vetch)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Pasture legumes</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Biserrula pelecinus</em></td>
<td>44–63</td>
<td>65</td>
<td>Field, maturity</td>
<td>21</td>
</tr>
<tr>
<td>(biserrula)</td>
<td></td>
<td></td>
<td>Soil, 49–77 d</td>
<td>29</td>
</tr>
<tr>
<td><em>Coronilla varia</em></td>
<td>5–21</td>
<td>76–160</td>
<td>Soil, various P,</td>
<td>15</td>
</tr>
<tr>
<td>(crown vetch)</td>
<td></td>
<td></td>
<td>60–64 d</td>
<td></td>
</tr>
<tr>
<td><em>Lespedeza stipulacea</em></td>
<td>73–139</td>
<td></td>
<td>Field survey,</td>
<td>25</td>
</tr>
<tr>
<td>(Korean lespedeza)</td>
<td></td>
<td></td>
<td>flowering stage</td>
<td></td>
</tr>
<tr>
<td><em>Lotus corniculatus</em></td>
<td>72–110</td>
<td></td>
<td>Field survey,</td>
<td>25</td>
</tr>
<tr>
<td>(sweet clover)</td>
<td></td>
<td></td>
<td>flowering stage</td>
<td></td>
</tr>
<tr>
<td>(sweet clover)</td>
<td></td>
<td></td>
<td>flowering stage</td>
<td></td>
</tr>
<tr>
<td><em>Medicago murex</em></td>
<td>47–92</td>
<td>64–131</td>
<td>Solution, 28–84 d</td>
<td>30</td>
</tr>
<tr>
<td>(medic)</td>
<td>209(^a)</td>
<td>185</td>
<td>Soil, 49–77 d</td>
<td>29</td>
</tr>
<tr>
<td><em>Medicago polymorpha</em></td>
<td>24–64</td>
<td>76–180</td>
<td>Solution, during</td>
<td>14</td>
</tr>
<tr>
<td>(medic)</td>
<td></td>
<td></td>
<td>d 40–61</td>
<td></td>
</tr>
<tr>
<td><em>Medicago polymorpha</em></td>
<td>188(^a)</td>
<td>164</td>
<td>Solution, during</td>
<td>14</td>
</tr>
<tr>
<td>(medic)</td>
<td></td>
<td></td>
<td>day 40–61</td>
<td></td>
</tr>
<tr>
<td><em>Medicago sativa</em></td>
<td>147–143</td>
<td>101–127</td>
<td>Soil, 131–167 d</td>
<td>22</td>
</tr>
<tr>
<td>(lucerne)</td>
<td></td>
<td></td>
<td>(2–3 cuttings)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120, 160</td>
<td>107–130</td>
<td>Field survey</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>145, 105</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>141–187</td>
<td>141–169</td>
<td>Solution, 28–84 d</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Field survey,</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>flowering stage</td>
<td></td>
</tr>
<tr>
<td><em>Medicago truncatula</em></td>
<td>186(^a)</td>
<td>156</td>
<td>Solution, during</td>
<td>14</td>
</tr>
<tr>
<td>(medic)</td>
<td></td>
<td></td>
<td>day 40–61</td>
<td></td>
</tr>
</tbody>
</table>

(continues)
TABLE 1  Continued.

<table>
<thead>
<tr>
<th>Species</th>
<th>Acid production (cmol kg(^{-1}) shoot)</th>
<th>EB (cmol kg(^{-1}))</th>
<th>Growth conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Ornithopus</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>compressus</em></td>
<td>143(^a)</td>
<td>163</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
<tr>
<td>(yellow serradella)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Ornithopus</em></td>
<td>78–128</td>
<td>86–158</td>
<td>Soil, 49–77 d</td>
<td>29</td>
</tr>
<tr>
<td><em>sativus</em> (pink</td>
<td></td>
<td>93</td>
<td>Field, maturity</td>
<td>21</td>
</tr>
<tr>
<td>serradella)</td>
<td></td>
<td>93–163</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>186(^a)</td>
<td>204</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
<tr>
<td><em>Stylosanthes</em></td>
<td>82–123</td>
<td></td>
<td>Field</td>
<td>7</td>
</tr>
<tr>
<td>spp. (stylos)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td></td>
<td></td>
<td>Field survey,</td>
<td></td>
</tr>
<tr>
<td><em>hybridum</em></td>
<td></td>
<td></td>
<td>flowering stage</td>
<td></td>
</tr>
<tr>
<td>(alsike clover)</td>
<td>128–144</td>
<td>129–137</td>
<td>Solution, 28–84 d</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106–152</td>
<td>Field survey,</td>
<td>25</td>
</tr>
<tr>
<td><em>pratense</em></td>
<td>180, 150</td>
<td>180, 105</td>
<td>flowering stage</td>
<td>32</td>
</tr>
<tr>
<td>(red clover)</td>
<td></td>
<td></td>
<td>Solution, 44 and 75 d</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td>120, 190</td>
<td>185, 165</td>
<td>Solution, 44 and 75 d</td>
<td>34</td>
</tr>
<tr>
<td><em>repens</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(white clover)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td>180(^a)</td>
<td>177</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
<tr>
<td><em>vesiculosum</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td>190(^a)</td>
<td>182</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
<tr>
<td><em>balansae</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td>211(^a)</td>
<td>235</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
<tr>
<td><em>glomeratum</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td>55–116</td>
<td>85–124</td>
<td>Soil, 49–77 d</td>
<td>29</td>
</tr>
<tr>
<td><em>tomentosum</em></td>
<td>265(^a)</td>
<td>255</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
<tr>
<td><em>Trifolium</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>subterraneum</em></td>
<td>45</td>
<td></td>
<td>Soil, maturity</td>
<td>21</td>
</tr>
<tr>
<td>(subterranean</td>
<td></td>
<td>75, 93</td>
<td>Soil, 82 and 105 d</td>
<td>26</td>
</tr>
<tr>
<td>clover)</td>
<td></td>
<td></td>
<td>Field survey</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>52–68</td>
<td>76, 97</td>
<td>Soil, various K, 55 d</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>28–57</td>
<td>92–140</td>
<td>Soil, various P, 60–64 d</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>83–100</td>
<td>91–146</td>
<td>Soil, 61–65 d</td>
<td>34, 35</td>
</tr>
<tr>
<td></td>
<td>188–214(^a)</td>
<td>178–193</td>
<td>Solution, during day 40–61</td>
<td>14</td>
</tr>
</tbody>
</table>

(continues)
The role of plant cation/anion uptake ratio is also influenced by plant age, the part of the plant under consideration, and edaphic and climatic conditions [25].

### 2.2.3 Ash Alkalinity

As opposed to determining excess cations, a simpler alternative method of measuring cation/anion balance in the plants is to measure the ash alkalinity in these tissues. The measurement of ash alkalinity involves the ignition of ground plant materials at 400 to 500°C and the titration of the produced ash with acid to determine the alkalinity caused by excess base cations present in the ash. In the ashing process, organic materials are combusted to volatile gases and the nonvolatile ions remain as alkaline carbonates with small amounts of phosphates and sulfates. However, with ashing at high temperatures, volatile sulfur and chlorine compounds may be lost during combustion [36] and thus may cause relatively higher ash alkalinity.

The ash alkalinity (AA) measured in this way is equal to the sum of the cations absorbed [\( \Sigma C^+ \)] minus the sum of the anions absorbed [\( \Sigma A^- \)] plus the amount of NO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) reduced and minus the amount of NH\(_4\)\(^+\) metabolized into uncharged forms [35], that is;

\[
AA = [\Sigma C^+] + [NH_4^+_{\text{absorbed}}] - [\Sigma A^-] - [NO_3^-_{\text{absorbed}}] + [NO_3^-_{\text{reduced}}] + [SO_4^{2-}_{\text{reduced}}] - [NH_4^+_{\text{metabolized}}]
\]

### TABLE 1  Continued.

<table>
<thead>
<tr>
<th>Species</th>
<th>Acid production (cmol kg(^{-1}) shoot)</th>
<th>EB (cmol kg(^{-1}))</th>
<th>Growth conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vicia villosa</strong></td>
<td>136–223</td>
<td>130–182</td>
<td>Solution, 28–84 d</td>
<td>30</td>
</tr>
<tr>
<td>(crown vetch)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cereal crops</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Avena sativa</em></td>
<td>48–76</td>
<td>Field survey, flowering stage</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>(oats)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Hordeum vulgare</em></td>
<td>26–49</td>
<td>Field survey, flowering stage</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>(barley)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Sorghum bicolor</em></td>
<td>29–44</td>
<td>Field survey, flowering stage</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>(sorghum)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Triticum aestivum</em></td>
<td>25</td>
<td>Soil, 82 d, NH(_4)-N</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>(wheat)</td>
<td>26</td>
<td>Field, maturity</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25–37</td>
<td>Field survey, flowering stage</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50–51</td>
<td>Soil, 61 d, NH(_4)-N</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71–73</td>
<td>Soil, 61 d, NO(_3)-N</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td><strong>Zea mays</strong> (corn)</td>
<td>38–75</td>
<td>Field survey, flowering stage</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Acid production was calculated on a dry-weight basis of the whole plants (shoot plus roots).
If both NH₄⁺ and NO₃⁻ are completely converted to NH₃ and SO₄²⁻ reduction is negligible, ash alkalinity is equal to excess cations. Indeed, there is a nearly 1:1 relationship between ash alkalinity and excess cations [e.g., 14,37]. However, the relationship between ash alkalinity and excess cations can also differ for different plant species, which may relate to species differences in nitrogen and sulfur metabolism. For example, in a pot experiment, Tang et al. [20] reported close relationships between ash alkalinity and excess cations in eight legumes. However, ash alkalinity overestimated excess cations in Lupinus species, whereas the reverse was true for other temperate legumes.

2.3 Cation/Anion Balance and Soil Acidification

Plants can alter the rhizosphere pH and subsequently the pH of the bulk soil. The generation of rhizosphere acidity or alkalinity is directly related to the processes of ion uptake by plant roots. Rhizosphere acidification can occur when plants take up more cations than anions. Theoretically, if all the plant residues were returned in situ to the soil and no N losses or acid inputs occurred, net acidification of the soil would be zero because of the deacidifying processes occurring during decomposition of plant materials (see later). However, in most agricultural ecosystems where part of or sometimes even the whole plant is removed in harvest or returned to a different horizon in the soil profile, a portion of acidity created in the soil remains.

A well-nodulated legume often accumulates most of its N through N₂ fixation. The N₂-fixing plants take up more cations than anions because they do not rely on uptake of nitrate to satisfy most of their N requirement. Thus, net efflux of H⁺ into the rhizosphere occurs, resulting in a decrease in rhizosphere pH. This has been demonstrated in a number of studies, e.g., with Trifolium pratense (red clover) [33], Trifolium repens (white clover), Medicago sativa (alfalfa), Glycine max (soybean) [1], and pasture legumes [29]. Acid production due to excess cation uptake by N₂-fixing legumes may be considerable. Nyatsanga and Pierre [22] have shown that a yield of M. sativa of 10 t ha⁻¹ produced acidity in the soil equivalent to 600 kg CaCO₃ ha⁻¹. The amounts of acid generated by various N₂-fixing legumes grown in the glasshouse varied between 5 and 265 cmol H⁺ per kg of dry biomass produced (Table 1).

Acid production by nonleguminous species is largely dependent on the amount and proportions of NH₄⁺ and NO₃⁻ present in the soil or supplied as fertilizers and taken up by the plant. NH₄⁺ nutrition decreases the pH, whereas NO₃⁻ nutrition generally increases the pH of root media [38]. The extent of pH changes is also affected by plant species [20,34].

It should be kept in mind that soil acidity developing under crops in the field also depends on (1) total biomass production, (2) whether all or only part of the crop is removed in the harvest, (3) the extent of nitrate leaching after residue de-
composition and mineralization, and (4) the proportion of N absorbed in ammonium and nitrate forms. The more biomass produced, the more acidity generated by roots of the plants reliant on N₂ fixation or receiving NH₄⁺/H₂PO₄⁻-based fertilizers. The removal of seeds at harvest for cereal and pulse crops or a pasture under animal grazing would contribute to the development of soil acidity to a lesser extent than the removal of shoots. Large acidification is expected where nitrate leaching is severe. High rainfall, lack of plant uptake, and factors favoring nitrification enhance nitrate leaching. Application of NH₄⁺-based fertilizers increases and while application of NO₃⁻ decreases acidification [39] (see later).

If all N in a legume is obtained through N₂ fixation, growing such a species would increase the acidity of the root medium by the amount equivalent to the content of excess cations or ash alkalinity of the plant. When plants are reliant on soil N or fertilizer N, the acidity produced can be calculated according to the following equation [40]:

\[
\text{Acid production} = (C - A) + 0.946N_{\text{org}} - 2x - y
\]

where all parameters are in mmol per plant, \(C - A\) represents excess cations, \(N_{\text{org}}\) is plant organic N, and \(x\) and \(y\) represent the organic N derived from NO₃⁻ and N₂ fixation, respectively. By using this equation, the input of acid by a crop growing in the field can be calculated.

3 FACTORS INFLUENCING CATION/ANION UPTAKE RATIO AND ACID PRODUCTION

3.1 Plant Species

Striking differences in acid production and capacity to acidify soils exist between plant species growing under same conditions. Generally, legumes cause more soil acidification than nonleguminous species. For example, when supplied with nitrate, *Fagopyrum esculentum* (buckwheat) and *Cicer arietinum* (chickpea) had lower rhizosphere pH than *Triticum aestivum* (wheat) and *Zea mays* (corn) [10,41]. These differences reflected differences in the cation/anion uptake ratios [42]. In a pot experiment with a brown podzolic soil, growing N₂-fixing plants of *Trifolium pratense* resulted in a pH drop from 7.2 to 4.5 after 14 months of growth, whereas ryegrass supplied with NH₄NO₃ hardly changed the pH during the same period [33]. In the field, the legume phase in the rotation has caused greater soil acidification than the cereal crop phase (Table 2).

More soil acidification under legumes than under other species may be attributed to greater excretion of protons due to greater excess cation uptake during N₂ fixation (which minimizes the need for nitrate uptake) or less ability to take up soil nitrate during growth. In addition, legume residues contain high N, resulting in large amounts of nitrate produced during residue decomposition (e.g., *Lupinus*...
The leaching of NO$_3^-$ is often 8- to 10-fold greater under leguminous pastures than under grass pastures [46]. In a field study, van Miegroet and Cole [47] reported that only 10 moles of nitrate per hectare per year was leached from the 40-cm layer under *Pseudotsuga menziesii* (Douglas fir), whereas 3640 moles per hectare per year passed that layer under leguminous *Alnus glutinosa* (red alder) forest. As a consequence, the A horizon was more acidified under *A. glutinosa* than under *P. menziesii* over the 50-year period.

Species differences in the extent of acidification exist among legumes. In glasshouse studies, acid production by N$_2$-fixing legumes ranged from 5 to 265 cmoles of H$^+$ per kg biomass produced (Table 1). Among temperate grain legumes, *Cicer arietinum* and *Lupinus angustifolius* have a greater acidifying ability than other species. Among pasture legumes, ranking varies between studies, but *Trifolium tomentosum* (woolly clover), *Trifolium pratense*, and *Trifolium subterraneum* (subterranean clover) generally have greater acidifying ability than *Ornithopus* spp. (serradella) and *Biserrula pelecinus* (biserrula).

In a sandy soil with no fertilizer NO$_3^-$ added, the amounts of H$^+$ produced

<table>
<thead>
<tr>
<th>Cropping system</th>
<th>Soil type</th>
<th>Acidification rate</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>39-year-old pasture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clover</td>
<td>Podzolic soil</td>
<td>2.00</td>
<td>43</td>
</tr>
<tr>
<td>Phalaris</td>
<td></td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>15-year rotation trial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Continuous lupin</td>
<td>Sandy loam</td>
<td>5.26</td>
<td>4</td>
</tr>
<tr>
<td>Lupin: wheat</td>
<td>Podzolic</td>
<td>4.11</td>
<td></td>
</tr>
<tr>
<td>Continuous wheat</td>
<td></td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td>Fenceline survey</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lupin + weeds</td>
<td>Sandy soils</td>
<td>0.55</td>
<td>5</td>
</tr>
<tr>
<td>Lupin: wheat</td>
<td></td>
<td>0.29–0.37</td>
<td></td>
</tr>
<tr>
<td>Wheat: 2 clover phases</td>
<td></td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Clover + weeds</td>
<td></td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Unimproved pasture</td>
<td></td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>25-year rotation trial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Continuous clover</td>
<td>Duplex soil</td>
<td>0.92</td>
<td>44</td>
</tr>
<tr>
<td>2 clover: wheat</td>
<td></td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Clover: wheat</td>
<td></td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Continuous wheat</td>
<td></td>
<td>0.35</td>
<td></td>
</tr>
</tbody>
</table>
per unit biomass varied more than twofold among eight species tested, with *Cicer arietinum* producing the highest and *Pisum sativum* (field pea) the lowest amount of H⁺ (Fig. 1). Such species variation was even greater when fertilizer NO₃⁻ was applied.

N₂-fixing tropical legumes, with generally lower excess uptake of cations over anions than temperate legumes, have a lower acidifying effect on the rhizosphere and the bulk soil [48]. In addition, the products of N assimilation in tropical legumes appear to be ureides (allantoin and allantoic acid), which have high pKₐ values and are therefore unlikely to be dissociated to donate protons at physiological pH values in the cytoplasm and the xylem [49].

In a range of legume species supplied with NO₃⁻-N as the only N source, the degree of change in the rhizosphere pH depends strongly on the geographic origin of the species [50]. In those originating from acid soils of the humid tropics (e.g., *Glycine max*), no appreciable rhizosphere acidification was found, in contrast to moderate acidification by species from temperate climates (e.g., *Pisum sativum*) and strong acidification by species from semiarid climates (*Cicer arietinum* and *Lens culinaris* (lentil)). This has important implications for species selection for soils at high risk of acidification.

**FIGURE 1** Proton excretion rates of eight grain legumes grown at 0, 5.7, 14, and 57 mg N kg⁻¹ soil as Ca(NO₃)₂. (Adapted from Ref. 20.)
3.2 Form of Nitrogen

The form of nitrogen supply plays a key role in the cation-anion relationship in plants and hence in net acid production. \( \text{NH}_4^+ \)-fed plants are characterized by a high cation/anion uptake ratio, whereas \( \text{NO}_3^- \)-fed plants have a low cation/anion uptake ratio. By comparison, legumes reliant on \( \text{N}_2 \) fixation are characterized by a cation/anion ratio greater than 1 (as discussed earlier). For instance, the cation/anion uptake ratios in *Alnus glutinosa* were 3.6–7.0 for plants reliant on \( \text{NH}_4^+ \), 0.4–0.5 for plants supplied \( \text{NO}_3^- \) and 2.1–2.2 for \( \text{N}_2 \)-fixing plants during 6 weeks of growth [40].

The acid generated by \( \text{N}_2 \)-fixing legumes was estimated to range from 0.2 to 1.6 moles of \( \text{H}^+ \) per mole N fixed, whereas the uptake and assimilation of 1 mole of \( \text{NH}_4^+ \) are associated with the excretion of 1.1 to 1.6 moles of \( \text{H}^+ \) [51]. In contrast, uptake and assimilation of \( \text{NO}_3^- \) involve \( \text{OH}^- \) efflux or \( \text{H}^+ \) influx. The amount of \( \text{OH}^- \) produced is close to 1 mole per mole of \( \text{NO}_3^- \) if \( \text{NO}_3^- \) is entirely assimilated in roots but ranges from 0 to 1 mole per mole of \( \text{NO}_3^- \) if \( \text{NO}_3^- \) is assimilated in shoots [49]. An addition of N as anhydrous ammonia, aqua-ammonia, or urea is not acidifying if the entire amount of added N is utilized by the plant. The increased soil acidification associated with \( \text{NH}_4^+ \)-N nutrition and \( \text{N}_2 \) fixation and increased alkalization associated with \( \text{NO}_3^- \) nutrition have been demonstrated in glasshouse experiments [e.g., 34] and in field studies [e.g., 8,39]. One should also bear in mind that \( \text{NH}_4^+ \)-N in soil may undergo nitrification, an acid-producing process in itself, with an added problem of subsequent leaching of the nitrate causing topsoil acidification.

The increased soil acidification associated with \( \text{NH}_4^+ \) nutrition and \( \text{N}_2 \) fixation and increased alkalization associated with \( \text{NO}_3^- \) nutrition have been demonstrated in glasshouse experiments [e.g., 34] and in field studies [e.g., 8,39]. One should also bear in mind that \( \text{NH}_4^+ \)-N in soil may undergo nitrification, an acid-producing process in itself, with an added problem of subsequent leaching of the nitrate causing topsoil acidification.

The balance between amounts of \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) present in soil also greatly influences the relationship between acid production in soil and accumulation of excess cations in the plant. \( \text{NH}_4^+ \) uptake increases soil acidification (due to \( \text{NH}_4^+ /\text{H}^+ \) exchange) but decreases the plant concentration of excess cations or ash alkalinity, whereas the opposite applies to \( \text{NO}_3^- \) [e.g., 34,35,52]. Increasing supply of \( \text{NO}_3^- \) decreases soil acidification (due to \( \text{H}^+ \) being taken up or \( \text{OH}^- /\text{HCO}_3^- \) extruded as \( \text{NO}_3^- \) is taken up) but increases plant ash alkalinity or the concentration of excess cations. In other words, there is a negative correlation between acid production and excess cations in plants of a given species when supplied with various amounts of \( \text{NO}_3^- \) [e.g., 20].

The increased excess cations or ash alkalinity present in the plants supplied with \( \text{NO}_3^- \) has an important implication. When returned to the soil and decomposed, residues containing high ash alkalinity or excess cations have a greater “liming effect” than residues containing low ash alkalinity [21,37]. Thus, a plant species that has a greater ability to use soil \( \text{NO}_3^- \) not only produces less acidity during the growing season but also neutralizes more acidity when its residues are returned to the soil and decomposed.
3.3 Nutrient Supply

Nutrient deficiencies can change the cation/anion uptake ratio and the pattern of \( H^+ \) excretion by the root system. In legumes, deficiency of nutrients such as Ca, P, Co, Cu, and Fe [53], which are directly involved in nodulation and nodule function, may also influence acid production indirectly through affecting \( N_2 \) fixation.

The increase in the rhizosphere acidification is a widespread phenomenon of root response to P deficiency in many plant species [54]. For example, when *Brassica napus* (oilseed rape) plants were grown in a P-deficient soil with an initial pH of 6.1, an increase in the rhizosphere pH was associated with excess anion uptake and a decrease of P concentration in the rhizosphere soil solution during the first 2 weeks. Thereafter, a decrease in rhizosphere pH was observed. This decreased rhizosphere pH was associated with excess cation uptake that probably resulted from decreased uptake rates of \( NO_3^- \) and increased uptake rates of Ca and Mg [55–57]. Similar responses in terms of rhizosphere acidification and cation/anion uptake ratio have been observed in *Helianthus annuus* (sunflower) under P deficiency [58].

In other instances, P deficiency–induced rhizosphere acidification is related to the extrusion of organic acids. However, the significance of organic acid extrusion in rhizosphere acidification is not clear. The pH decrease of the rhizosphere soil under \( NO_3^- \)-fed *Lupinus albus* grown in a P-deficient calcareous soil was explained by the excretion of a large amount of citric acid [59]. By contrast, Gardner et al. [60] observed that large quantities of citrate were extruded from cluster (proteoid) roots of P-deficient *L. albus* grown in a mix of sand and vermiculite and that the exudates were neutral in pH because they were citrate anions rather than citric acid. In a sandy soil of pH 5.4, the contribution of organic acids to total acidification appeared to be small under P-deficient *L. albus* and *Cicer arietinum* [15].

Potassium is the most abundant essential cation in higher plants. In charge compensation, \( K^+ \) is the dominant cation for counterbalancing organic and inorganic anions in plants [16]. However, application of \( K_2SO_4 \) to a K-deficient acidic sand decreased the amount of acidity left in the soil by *Lupinus angustifolius* and *Trifolium subterraneum* per unit biomass produced. Under K deficiency, Ca uptake increased, which led to an increase in excess cation uptake and thus the specific acid production [27].

Dicotyledonous and nongrass monocotyledonous plant species deficient in Fe can induce rhizosphere acidification [61]. However, the effect of Fe deficiency may be of little importance to soil acidification because Fe deficiency generally occurs in high-pH soils. Under Zn deficiency, the rhizosphere acidification by dicotyledonous plants occurs only when the deficiency becomes severe. In *Gossypium hirsutum* (cotton), *Fagopyrum esculentum*, and *Helianthus annuus* grown in nutrient solution with nitrate as the only nitrogen source, the solution pH de-
creased from 6 to 5 under Zn deficiency, whereas the pH increased from 6 to 7 when plants were adequately supplied with Zn. In Zn-deficient plants, excretion of net excess H\(^+\) was associated with a shift in the cation/anion uptake ratio in favor of cation uptake, while nitrate uptake was drastically decreased [62].

### 3.4 pH

Soil acidity can markedly decrease root growth and nutrient uptake and alter the cation/anion uptake ratio. Low pH generally decreases cation uptake but does not affect or stimulate anion uptake. Hence, low pH decreases excess cation uptake and consequently H\(^+\) excretion. The net H\(^+\) efflux from roots of *Medicago sativa*, *Trifolium pratense*, and *Trifolium repens* grown for 75 days in the flowing solution culture was not affected by pH between 4.75 and 6.75, but there was an immediate cessation of H\(^+\) excretion when the solution pH was adjusted to 3.75 [32]. Similar effects of low pH have also been found in *Pisum sativum*, with net proton excretion being 2.3 times higher at pH 7 than at pH 4 over the 6-week period [28]. A greater net acidification rate under pasture was recorded for soils with higher initial soil pH [63].

### 4 CATION/ANION UPTAKE RATIO AND SUBSOIL ACIDIFICATION

Studies in Australia have shown that soil acidification in legume-based agriculture is occurring not only in the topsoil but also in the subsoil to a depth of more than 80 cm [3–6,8,64]. For example, in the central wheatbelt of Western Australia, soil pH increased with increasing depth in the uncleared (native vegetation) sites, whereas with the cleared (farming) sites the lowest pH occurred in the 10- to 20-cm layer; below this layer, the pH increased with depth. Soil pH below the 10-cm depth declined linearly with years of clearing, with an average annual rate of 0.007 unit [6]. Although the cause of subsoil acidification is not yet fully understood, recent studies suggest that acid production by plant roots due to excess cation uptake plays an important role in the development of subsoil acidification [26].

Where in the soil profile acidity generated during plant growth is deposited depends on the distribution of the roots and nutrients, the pattern of nutrient uptake and H\(^+\) extrusion along the roots, and the amount and distribution of plant residues returned to the soil. The pattern of H\(^+\) excretion along the root of *Helianthus annuus*, *Lupinus angustifolius*, and *Pisum sativum* with a sufficient supply of nutrients was generally uniform [65,66]. By contrast, H\(^+\) extrusion was higher near the root elongation zone than in other root zones in *Zea mays* [67,68]. The H\(^+\) was excreted at the basal portion of *Triticum aestivum* roots supplied with NH\(_4\)^+ [69], and OH\(^-\) was excreted at the basal portion of the taproot where laterals had initiated [50] or at the root apex [70] of *Z. mays* receiving NO\(_3\)^-. In a soil
column experiment in which N$_2$-fixing \textit{L. angustifolius} and \textit{Trifolium subterraneum} were grown, the decrease in pH down the soil profile was proportional to the root length density [26].

The pattern of H$^+$ excretion along the root is also influenced by the distribution of nutrients. Using a split-root technique, Römheld [50] demonstrated that \textit{Zea mays} roots supplied with NH$_3^+$ acidified the rhizosphere, whereas those fed with NO$_3^-$ increased the rhizosphere pH. Loss et al. [19] reported that up to twice as much H$^+$ was excreted in root zones of nodulated \textit{Lupinus angustifolius} where 1.2 mM K was applied than in zones where K was not supplied. Similarly, Ohwaki et al. [71] showed that the presence of cations in the nutrient solution is required for proton exudation in order for nonspecific H$^+$/cation antiport to function in roots of \textit{Cicer arietinum}. More recently, C. Allmark et al. (unpublished) showed that greater acidification occurred in the root zone of N$_2$-fixing \textit{L. angustifolius} where full nutrients (without N) were supplied than in the zone receiving Ca and B only. The amounts of H$^+$ released in different root zones were related to excess uptake of cations over anions.

Nutrients may be distributed unevenly in soils, both vertically and horizontally. The uneven supply of nutrients along the root axis can markedly affect root distribution and proliferation, which in turn influence the pattern of H$^+$ extrusion in the soil profile. Root growth is stimulated by localized supply of nutrients or in a nutrient-rich zone [72]. Over a threefold increase in root growth was observed in \textit{Hordeum vulgare} in response to a localized supply of P [73]. In a soil column study in which basal nutrients were applied only to the top 10 cm, 60–70% of the total root length of \textit{Lupinus angustifolius} and over 50% of \textit{Trifolium subterraneum} were distributed in that layer. By comparison, root length density tended to increase with depth when the nutrients were applied uniformly throughout the column [26]. The effect of localized nutrient supply in enhancing root growth has been suggested to be controlled by the apical root meristem and supply of carbon assimilates [74].

Plant species differ greatly in root morphology (diameter, density, etc.) and root distribution in the soil profile and therefore display different patterns of nutrient uptake and H$^+$ excretion along the root axis as well as down the soil profile. Dicotyledons have a main taproot with fewer laterals, whereas monocotyledons have a fibrous root system [75]. Grain legumes usually have a deeper root system than pasture legumes and acidify deeper soil layers when excess uptake of cations over anions occurs. On deep yellow sands in the Western Australian wheatbelt, the average root diameter of \textit{Lupinus angustifolius} was 0.5 mm, about twice that of \textit{Trifolium subterraneum} or \textit{Triticum aestivum}. Of the total root length, 40% for \textit{L. angustifolius}, 51% for \textit{T. aestivum}, and 70% for \textit{T. subterraneum} occurred in the top 20 cm of soil [76]. Indeed, in a field survey, Loss et al. [5] observed more soil acidification in deeper layers of soil profiles under lupin–wheat rotation than under pastures.
The deposition and decomposition of plant residues do not cause subsoil acidification but contribute to the development of the soil pH profiles through the alkalization effect in the topsoil. Indeed, addition of plant residues to acidic soils has been demonstrated to increase soil pH. The magnitude of this pH increase (alkalinity production) in soil depends on the type of plant materials added, the rate of their breakdown, and the initial pH of the soil. Such alkalinity production was correlated positively with the concentration of ash alkalinity or excess cations in the residues [21,37,77] and negatively with the initial soil pH [21]. The increase in soil pH due to the residue addition has been attributed to (1) the decarboxylation of organic anions [78], (2) accumulation of NH$_4^+$ [79] and release of NH$_3$ during the decomposition of organic N [80], (3) production of OH$^-$ by the ligand exchange between the terminal OH$^-$ groups of aluminum and iron hydroxy-oxides and organic anions [81], (4) production of OH$^-$ by reduction of Mn and Fe oxides under reducing conditions [81], and (5) an increase in soil base saturation through the replacement of protons and Al from exchange sites by cations coming out of the decomposed plant residues [82].

Although the extent of proton excretion from roots during plant growth is proportional to the root distribution, oxidation of organic anions during decomposition of the shoot residue mainly occurs in the topsoil because residues are generally not incorporated into deeper layers. Thus, the decomposition of shoot residues neutralizes the acid created during plant growth in the topsoil. In some soils where subsoil acidification has occurred, an increased soil pH with time of farming can be observed in the top layer. Root residues usually have less excess cations than shoot residues and have a lesser “liming” effect [21,77]. Therefore, root residue decomposition will not fully neutralize acidity created along the roots in the soil profile during the growth period, and acidity produced during growth will persist in the subsoil layers.

Although nitrification coupled with nitrate leaching is a major source of protons for topsoil acidification (see Chapter 2), it is not a cause of subsoil acidification because mineralization and nitrification of plant residue N occur mainly in the topsoil. For instance, 64% of N mineralization and 50% of nitrification in the soil profile of a loamy sand and 78% of N mineralization and 41% of nitrification in a sandy clay loam occurred in the top 5-cm soil layer [83]. Similarly, Young et al. [84] observed that nitrification was negatively correlated with soil depth in the surface 10 cm. Production of nitrate results in excess protons in the topsoil (where nitrification occurs). If the nitrate is taken up by plant roots in the topsoil, there is no net acidification. If the nitrate is leached, soil acidification then occurs in the topsoil layer. The uptake of the leached nitrate by plant roots in subsoil layers is accompanied by extrusion of OH$^-$/HCO$_3^-$ and thereby reduces subsoil acidification [26].

Figure 2 summarizes possible causes of subsoil acidification. The acid produced during plant growth due to excess cation uptake makes a major contribution
to the development of the acidity profile. The amount of acid generated by plant roots is proportional to the root distribution. The oxidation of organic anions present in the residues, an alkalinization process, however, occurs mainly in the topsoil and thus neutralizes only the acidity produced by plant growth in that layer. Therefore, the acidity in the subsoil persists. Leaching of nitrate that originated from nitrification of the residue N causes topsoil acidification. When leached nitrate is taken up in the subsoil, a portion of acidity generated by the root during plant growth is neutralized. Finally, the downward movement of H⁺ and soluble Al [85], and NH₄⁺ may potentially contribute to the development of subsoil acidification, but knowledge of the magnitude of leaching of these acidic components is meager at present.

5 MINIMIZING SOIL ACIDIFICATION THROUGH MANAGING CATION/ANION UPTAKE

This section provides some ideas on how acidification of soil, and especially subsoil, may be minimized through management of cation/anion uptake (see also Chapter 2). Detailed information on the amelioration of soil acidity by other means is covered in Chapters 11 and 12.

5.1 Maximize Nitrate Uptake

Whereas subsoil acidification appears to result mainly from excess cation over anion uptake by roots, nitrate leaching from topsoil is a major cause of topsoil acidification. In a grass–legume pasture, Helyar and Porter [2] estimated that the oxidation (mineralization and nitrification) of organic N and subsequent leaching of NO₃ contributed to 40% of (top)soil acidification. Nitrate concentration can be as
high as 10 mM in the soil solution below 15 cm in sandy soils [5]. As discussed earlier, nitrate uptake by the plant is a deacidifying process. Thus, the efficient use of soil nitrate by plant roots in deeper layers during the downward movement of nitrate reduces subsoil acidification. The resultant topsoil acidification can easily be ameliorated by liming or through shoot residue decomposition.

Tang et al. [26] demonstrated that uptake in the subsoil of nitrate leached from the topsoil indeed decreased subsoil acidification under *Lupinus angustifolius*, *Trifolium subterraneum*, and *Triticum aestivum*. In 1-m soil columns where basal nutrients were applied uniformly throughout the column, root length density of the plants was relatively uniform below 10 cm. The addition of (NH$_4$)$_2$SO$_4$ in the top 10 cm increased NO$_3$ concentration in all layers, but NH$_4$ was mainly retained in the top 30-cm layer. Compared with the N$_2$-fixing plants, the plants of *L. angustifolius* and *T. subterraneum* grown with (NH$_4$)$_2$SO$_4$ in 0–10 cm of the column caused more acidification in the top 10 cm but less acidification in the 10–50-cm depth. *Triticum aestivum* grown in columns with (NH$_4$)$_2$SO$_4$ in 0–10 cm increased soil pH below the 20-cm depth.

Plant species differ greatly in their ability to intercept NO$_3$ as it is being leached down the soil profile. In the field, NO$_3$ leaching was much greater under *Lupinus angustifolius* than under *Triticum aestivum* [86]. In a pot experiment with eight nodulated grain legume species (Fig. 1), increasing nitrate supply up to 57 mg N kg$^{-1}$ soil increased nitrate uptake by 40 to 77% (the highest increase in *Lathyrus sativus* and the lowest in *Lupinus albus*). Accompanying an increase in nitrate uptake, proton excretion declined by 45 to 100% (the highest decrease under *L. sativus* and the lowest under *Cicer arietinum*). Genotypes within the same species may also differ in utilizing soil NO$_3$ (e.g., genotypes of *Pisum sativum* [87]). Moreover, Bowman et al. [88] showed that less nitrate was leached under deep-rooted than shallow-rooted than shallow-rooted genotypes of *Agrostis palustris* (bentgrass) and suggested that root architecture (distribution and density) is important in uptake of leached nitrate in soil profiles. Selection of species and genotypes that produce acid the least and use soil NO$_3$ to the greatest extent may provide an option for minimizing subsoil acidification. This would also reduce topsoil acidification if uptake of nitrate occurs in the topsoil.

Replacement of annual pastures with perennial pastures has a potential to reduce nitrate leaching. The nitrate leached under the pasture was reduced by half or more by establishing perennial grasses with *Trifolium subterraneum* [43]. Higher soil pH values have been measured under the *Phalaris*-based pasture than under a comparable annual grass/subclover-based pasture, with the net acid addition to the soil being 0.7 kmol ha$^{-1}$ year$^{-1}$ lower under the *Phalaris* pasture [43].

Compared with acid-sensitive species, growing acid-tolerant species and genotypes on acidic soils usually leads to increased root growth, especially into acidic subsoils [89]. Such greater root density in the subsoil will increase the capacity of roots to absorb nitrate leached from the nitrification zone.
Subsoil acidification can be decreased through the management of N fertilizers. The application of nitrate fertilizers increased the pH of acid subsoils under perennial grasses [90]. More recently, Noble et al. [7] proposed that the formation of Ca(NO₃)₂ through the application of lime and NH₄_/H₂O₄-based fertilizers, subsequent nitrate leaching into, and the preferential uptake of NO₃ in the subsoil offer a feasible and practical method for ameliorating subsoil acidity in sugarcane production.

5.2 Minimize Alkalinity Removal and Redistribution

Removal of any parts of the plant from the field will decrease alkalinity at the site and may cause permanent soil acidification. However, different plant parts contain various amounts of excess cations (see also Chapter 5). Leaves generally have a higher excess cation concentration than stem. Shoots have more excess cations than roots, which in turn have more than seeds [13,14,21,25]. The removal of seeds would therefore cause less acidification than removal of shoots. The acidifying effect of plant growth is greater when the plant is cut for hay or silage and the plant material removed than under a grazed pasture where the proportion of alkalinity returned in the form of animal excreta is relatively large [1].

As discussed earlier, legumes usually have a greater capacity to excrete protons and less ability to take up nitrate during growth compared with cereals. They also have higher excess cations or ash alkalinity in their tissues (Table 1) and thus higher amounts of alkalinity can be removed in their products. A decrease in the proportion of legumes in the rotation would thus reduce soil acidification. However, this is likely to have adverse effects on overall production and profitability in many agricultural regions because of a lack of input of N fixed by legumes. Alternatively, selection of legume species with low excess cations or ash alkalinity in the products is an option.

5.3 Impact of Trees and Shrubs

Trees and shrubs may play a role in minimizing soil acidification through the development of deep root systems capable of taking up bases such as Ca and Mg in deep layers of the soil profile and returning them to the topsoil as leaf litter containing excess cations or ash alkalinity. Furthermore, trees and shrubs, with their deeper rooting patterns and perennial nature, have a potential to capture more soil nitrate than crops and annual pastures, thereby reducing nitrate leaching and decreasing net acid input. It should be noted, however, that the decrease of acidity in the topsoil due to leaf litter decomposition is at the expense of increased acidification in the deep soil layer.

Excess cations or ash alkalinity in leaf litter of trees ranged from 36 to 247 cmol kg⁻¹ [37]. Most eucalypt and acacia species and radiata pine had relatively low concentrations of ash alkalinity, whereas a number of northern hemisphere
deciduous species had higher ash alkalinity. *Milia azedarach* (white cedar), a native species of Australia’s east coast, had the highest ash alkalinity among the 16 species tested. An addition of the leaf litter materials to an acid red podzolic soil increased soil pH and decreased extractable Al; the increase in pH was proportional to the quantity of excess cations or ash alkalinity added [37].

Information on the effect of trees and shrubs on decreasing soil acidification in the field is limited. A field survey showed that the soil under tree and shrubs was less acidic than adjacent soil and had higher exchangeable cations and lower extractable aluminum [91]. Growing *Chamaecytissus palmensis* (tagasaste) on an acid soil resulted in a rise in the soil pH beneath the shrubs [92]. However, the increase in pH diminished 2 m away from the shrub row (C. Tang, unpublished).

## 6 CONCLUSIONS

Excess uptake of cations over anions by plant roots plays an important role in soil acidification, especially in the development of subsoil acidity. Plant species and genotypes differ substantially in concentrations of excess cations or ash alkalinity and their ability to produce acid and to utilize soil nitrate. Soil acidification under legumes is greater than under nonlegume crops because of (1) large excess uptake of cations over anions due to N₂ fixation and (2) the low capacity to take up nitrate once organic N is decomposed. Ammonium nutrition increases and nitrate decreases soil acidification under other crops. Whereas much emphasis has been placed on the amelioration of soil acidity, more efforts should be devoted to minimizing or preventing soil acidification and, especially, subsoil acidification. Selection of species and genotypes with low excess cations in the products, low acid production, and high capacity to take up soil nitrate may provide an option to minimize subsoil acidification. Perennial species may also play a role in this respect. Further, strategic use of N fertilizers with minimal NH₄⁺ leaching from the topsoil and maximal NO₃⁻ utilization in the subsoil may be considered.

## REFERENCES

Role of Plant Cation/Anion Uptake Ratio

66. PF White, AD Robson. Rhizosphere acidification and Fe$^{3+}$ reduction in lupins and peas: iron deficiency in lupins is not due to a poor ability to reduce Fe$^{3+}$. Plant Soil 119:163–175, 1989.
Role of Plant Cation/Anion Uptake Ratio 81

Acid Inputs into the Soils from Acid Rain

Christine Alewell
University of Bayreuth, Bayreuth, Germany

1 INTRODUCTION

Industrialized regions of the world have been confronted with the consequences of acidic deposition since the beginning of the 20th century. Today, there is substantial concern about the environmental impacts of air pollution on the local, regional, and global scale [1]. It has been shown that observed levels of various air pollutants can threaten human health, vegetation, wildlife, and soil biology; cause damage to materials; and change the chemistry of soils and waters.

The term “acid rain” or “acid deposition,” which covers the wide range of physical, chemical, and biological processes involved in the issues of acidification, is defined here as the acid input to ecosystems and soils from the atmosphere originating in human activity (e.g., in fossil fuel burning). Although there is some question of whether any location on the earth is untouched by human activities in some way, the natural troposphere is usually referred to as the atmosphere over remote areas [2]. Thus, the anthropogenic pollution of the atmosphere, which is the origin of acid rain, always has to be assessed in comparison with the natural troposphere.

Widespread regulatory action to curb air pollution was not taken until strong links were established between human health and pollutants in the mid-1900s. Until the 1950s, air pollution was emitted from relatively short smokestacks and had
the most profound effects in areas immediately surrounding the source. In urban areas throughout the world, pollution events were both severe and frequent enough during this time period that they often led to human health problems [3]. One smog event in London in 1952 reportedly caused 4000 deaths [4]. In an effort to ameliorate the urban pollution situation, smokestack height was increased in North America and Europe between the 1950s and 1970s so that pollutants would disperse more widely. With the increased stack height, local pollution became regional pollution, and the era of the long-range transport of acid deposition had started. Acid rain problems have also extended to Asia because of a significant increase in atmospheric emissions resulting from high economic and population growth [5].

The deleterious effects of acid rain on soils have much in common with those of acid produced naturally in soils; the active principles, acids in solution, are similar [6]. However, anthropogenic atmospheric deposition was shown to influence the biogeochemistry of forest ecosystems significantly and to accelerate soil acidification [7,8].

This chapter gives an overview of the forms and the origin of acidifying pollutants as well as deposition processes and their measurements. A short section deals with the consequences of acid deposition for ecosystems and their biota. The chapter ends with a discussion of long-term trends and the expected changes in acid deposition in the future.

2 ORIGIN AND FORMATION OF ACIDIFYING AIR POLLUTANTS

Once emitted, many air pollutants remain in the atmosphere for some time before they are finally deposited on the ground. During this time, they are transported with the air mass over long distances, often crossing national boundaries. As a consequence, at a given site, the concentration of pollutants and their deposition on the ground are influenced by a large number of emission sources, frequently from many different countries.

The processes of atmospheric deposition are complex and involve several different mechanisms in forms of wet (rain or snow) and dry deposition (aerosols including fog and cloud droplets, absorption of gases on wet surfaces, and deposition of dust particles). The complex interaction with forest canopies or leaves of plants is discussed in Sec. 3. However, it is important to keep in mind that these interactions already take part in transforming deposited substances before they reach the soil surface.

In the following, the primary cause of acid deposition, the emissions of nitrogen and sulfur compounds to the atmosphere, resulting in the formation of nitric acid (HNO₃) and sulfuric acid (H₂SO₄) and the deposition of ammonium (NH₄⁺), will be discussed. At the end of each section, a discussion of control tech-
niques and possible abatement strategies will be given. When discussing abatement strategies, it is important to keep in mind that North America as well as Europe has so far concentrated only on best available technologies to reduce emission of NO$_x$ or SO$_2$. However, nontechnical options, such as substitution of fuels (e.g., switch from high- to low-sulfur coal or oil), substitution of the energy carrier (switch from coal to oil to gas or increased share of renewables), and rational use of energy, have a great potential to reduce emissions at low costs [9]. The latter abatement strategies might become especially important for Northeast Asia (see Sec. 5.3).

2.1 Nitrogen

For the global nitrogen budget, Galloway [10] estimates 140 million tons of nitrogen per year to be mobilized just by human activities (80, 40, and 20 million tons from commercial fertilizer production, legume and rice cultivation, and fossil fuel combustion, respectively). Of these 140 million tons per year, only 80 million tones are emitted to the atmosphere: 20 million tons from fossil fuel combustion and 50 and 10 million tons per year from agricultural activities as ammonia (NH$_3$) and nitrogen oxide (NO$_x$), respectively [10]. Because sources and sinks of NH$_3$ and NO$_x$ differ significantly, they are discussed separately in the following.

2.1.1 NO$_x$

Nitric oxide (NO), nitrogen dioxide (NO$_2$), and nitrous oxide (N$_2$O, known as “laughing gas”) are collectively named NO$_x$. Other nitrogen oxides such as nitrogen trioxide (NO$_3$), dinitrogen trioxide (N$_2$O$_3$), dinitrogen tetroxide (N$_2$O$_4$), and dinitrogen pentoxide (N$_2$O$_5$) are also identified in the atmosphere, but they decompose to NO$_2$ by reacting with NO and/or by photolysis [11].

The NO$_x$ gases enter the atmosphere from natural and anthropogenic sources. The main oxidized nitrogen compound emitted is nitrogen monoxide, which is oxidized to nitrogen dioxide. The oxidation of NO$_2$ by OH is the major route of formation of nitric acid in the boundary layer of the troposphere:

$$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$$

The N$_2$O gas is relatively unreactive; however, its concentration decreases rapidly with altitude as a result of a photochemical reaction yielding dinitrogen and monatomic oxygen:

$$\text{N}_2\text{O} + \text{light} \rightarrow \text{N}_2 + \text{O}$$
$$\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$$
$$\text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO}$$
$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$
NO$_x$ plays a considerable role in the production of ozone in the troposphere [12]:

\[
\text{NO}_2 + h\nu(\lambda \leq 430 \text{ nm}) \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \text{ (increased energy)}
\]

in which M is another species, such as a molecule of N$_2$ or O$_2$, which absorbs the excess energy of the reaction and stabilizes the ozone molecule. The reaction is an important primary photochemical process initiating smog formation because the monatomic oxygen or the ozone produced reacts with hydrocarbons to produce highly reactive hydrocarbon free radicals. The hydrocarbon free radicals react further with species such as NO$_2$ to produce peroxycetyl nitrate, aldehydes, and other smog components.

The reaction sequence for O$_3$ production involves converting NO to NO$_2$ at a rate sufficiently high to maintain an NO$_2$/NO ratio to sustain the observed background levels of O$_3$ [12].

For the global NO$_x$ budget, Logan [13] gives sources amounting to a total of 25 to 99 million tons N per year versus sinks (precipitation and dry deposition) of 24 to 64 million tons N per year. Of the sources, 40% is attributed to fossil fuel combustion, 22% to burning of biomass, 15% to lightning, 15% to microbial activity in soils, and 1 to 10% to the chemical oxidation of ammonia [13].

In Europe, the sector “public power plants cogeneration and district heating” contributes 21% of the total NO$_x$ emission, 13% is produced by industrial combustion processes, and the remaining 65% is attributed to the transport sector [14,15]. Road transport accounts for the major part of the emissions from the transport sector (90%), with less than 3% from aviation and the remaining part from sea transport and inland waterways [15].

The most common approach in Europe and North America to reduce NO$_x$ emissions is to define technology, fuel, and pollutant-specific emission standards for the most relevant sources. The NO$_x$ emissions can be reduced by avoiding the formation of pollutants (primary measures) or by flue gas cleaning (secondary or end-pipe measures) [14]. Primary measures are based on lower combustion temperatures that lead to lower NO$_x$ formation. A further reduction is achieved by integrated emission control measures such as air staging and flue gas recirculation [14]. Secondary NO$_x$ techniques result in NO$_x$ reduction by adding nitrogenous agents such as ammonia or urea, which react with the nitric oxides to form nitrogen and water. An important development was the catalytic converter for automobiles in which platinum catalyzes the reaction of NO$_x$ to N$_2$ and CO to CO$_2$.

2.1.2 NH$_4$

Reduced nitrogen is present in the atmosphere almost entirely as gaseous NH$_3$ or particulate NH$_4^+$ (either solid or liquid droplets). Ammonia (NH$_3$) has a relatively short residence time in the atmosphere because it is rapidly converted to ammo-
nium (NH$_4^+$), thereby neutralizing acid pollutants (H$_2$SO$_4$, HNO$_3$, or HCl) in the air as well as in the water phase. Thus, the emission of ammonia is, strictly speaking, not a cause of acid rain. However, the conversion of NH$_4^+$ to either amino acids or NO$_3^-$ in soils is always connected with the production of acidity. The assimilation of NH$_4^+$ during production of amino acids produces 1 mole of protons per mole of NH$_4^+$_x:

\[
\text{NH}_4^+ + \text{R—OH} \rightarrow \text{R—NH}_2 + \text{H}_2\text{O} + \text{H}^+
\]

Nitrification of NH$_4^+$ to NO$_3^-$ is connected with the production of 2 moles of protons for each NH$_4^+$ molecule:

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+
\]

Furthermore, NH$_4^+$ deposition in ecosystems can cause substantial changes through eutrophication.

The main source of NH$_3$ is livestock farming (>90% in most countries [16]). The deposition of reduced nitrogen compounds is much more dependent on nearby point sources as nitrogen or sulfur oxides because of the short lifetime of NH$_3$ in the atmosphere [16] and the low emission height.

Estimates of total global NH$_3$ emissions are 109 to 131 million tons, of which 77 to 95 million tons are anthropogenically produced and 32 to 36 million tons are from natural processes [17]. Only around 10% of the anthropogenically produced NH$_3$ emissions are produced in North America and Europe. In Europe, the amount of N emitted as NH$_3$ is comparable to the amount emitted as NO$_x$ (6.5 and 7.1 million tons, respectively [18]). In the United States, 1 to 3 million tons of N are emitted as NH$_3$ [19].

More than 40% of ammonia emissions in Europe result from intensive pig, cattle, and poultry production (housing and storage), 35% from applied manure, 3 to 17% from fertilizer, and the remainder from industry and households [19–21]. For the United States, approximately 65% is attributed to livestock waste, 10% to fertilizer application, and 25% to industrial processes [19]. For Japan, the overall total NH$_3$ emission from livestock was given as 12 \times 10^5 tonnes NH$_3$ per year [22], which represents relatively small emissions compared with those of most European countries [22].

The main source of NH$_3$ within livestock farms is animal excreta. The conversion of feed N to animal product is often inefficient, and most of the N is excreted. A reduction of N in the animal diet or an increase in the efficiency of utilization of dietary N is one suggested means of reducing NH$_3$ emissions [20]. Techniques for the reduction of ammonia emission are mainly focused on reducing the NH$_3$-emitting area exposed to the air, reducing the NH$_3$ or NH$_4^+$ concentration in solution, or reducing the exchange of air above the emitting surface [20]. The various methods to reduce NH$_3$ emissions from animal houses (scraping slurry from the floor, adding water to the slurry, acidifying the slurry, implement-
ing filters in the ventilation system to clean the air) are not feasible because of either increased work time or increased costs [20]. Techniques to reduce NH₃ emissions from storage (covering slurry stores) or during application of slurry (using trail hoses or shallow injection) seem to be effective and feasible. There is a high rate of NH₃ loss from slurry immediately after field application (more than half of the total loss might occur during the first 6 days [23]). Thus, postapplication techniques (incorporation of slurry by ploughing or rotary harrow, irrigation with water or rain) must be brought into operation as quickly as possible if they are to be effective. Furthermore, the timing of the surface applications of slurry is important as losses are weather dependent. Because of the increase of NH₃ emissions with an increase in temperature, warm weather should be avoided. Unfortunately, this conflicts with the need for good trafficability of the soil and the desire for good crop-growing conditions.

Generally, the abatement strategies for NH₃ emissions are not easy to solve because of conflicts in economic interests and the side effects of some of the measures. For example, mixing deep litter in animal houses reduces NH₃ emission but causes high emission of the greenhouse gas nitrous oxide [24]. A further problem is the conflict with aiming at an environment beneficial to animals. For instance, tying animals during housing reduces the slatted floor area to which excreta is spread and has been shown to reduce NH₃ emissions by nearly 80% [24]. The latter conflict may be solved in some cases by increasing the proportion of the year during which the animals are allowed to graze, which would reduce the ammonia volatilization at the farm level and simultaneously increase economic benefits and animal welfare [20].

2.2 Sulfur

A number of gaseous sulfur compounds are emitted into the atmosphere through natural processes and/or anthropogenic activities. The most commonly known are sulfur dioxide (SO₂), hydrogen sulfide (H₂S), carbonyl sulfide (COS or OCS), dimethyl sulfide (CH₃SCH₃), methyl mercaptan (CH₃SH), carbon disulfide (CS₂), and dimethyl disulfide (CH₃SSCH₃) [11]. Of these, SO₂ is the dominant species (~95%) and of greatest environmental concern.

The largest part of the naturally emitted sulfur enters the atmosphere as H₂S [6]. The H₂S emitted into the atmosphere is converted to SO₂ within hours to days. The chemical reactions involved are complex but probably include free radical formation:

\[ \text{H}_2\text{S} + \text{O} \rightarrow \text{OH} + \text{HS} \]

The overall reaction would be

\[ 2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O} \]
The greater part of the anthropogenically produced sulfur originates from burning processes; thus, it enters the atmosphere as SO$_2$. Once in the atmosphere, SO$_2$ is oxidized to SO$_4^{2-}$ by homogeneous (gas to gas phase) or heterogeneous (gas to particle phase) reactions. The oxidation mechanism involves a complex photo-oxidation cycle (for details see Ref. 11), but according to Tanner [19] the principal gas-phase route for H$_2$SO$_4$ formation is

\[
\begin{align*}
SO_2 + OH^- & \rightarrow HSO_3 \\
HSO_3 + O_2 & \rightarrow SO_3 + HO_2 \\
SO_3 + H_2O & \rightarrow H_2SO_4
\end{align*}
\]

The overall reaction would be

\[
SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4
\]

The reaction represents a series of steps of somewhat uncertain nature. Normally, the rate of conversion of sulfur dioxide to sulfur trioxide is very slow. However, sunlight in a humid atmosphere appears to catalyze the reaction, and NO$_x$ is known to increase the rate of conversion.

A limited quantity of sulfates (SO$_4^{2-}$, SO$_3^+$, H$_2$SO$_4$) is directly emitted to the atmosphere by industrial processes such as petroleum refining, nonferrous smelting, pulp milling, and the manufacture of sulfuric acid [19].

It is estimated that, on a global scale, one half of the sulfur entering the atmosphere results from human activities, the other half from natural processes [25]. Each fraction approaches 100 million tons per year [26]. For the northern hemisphere, Cullis and Hirschler [27] give an estimation of 76 million tons in 1976 from natural sources versus 98 million tons from anthropogenic sources. For the southern hemisphere, they estimate 72 and 6 million tons for natural and anthropogenic sources, respectively [27].

The approximate percentage contributions of the main sources of natural sulfur emissions are as follows: volcanoes, 18%; open-ocean biogenic production, 46%; coastal zone and wetland biogenic sources, 3%; terrestrial plants and soils, 13%; biomass burning, > 4%; wind-raised dust, 16% [25]. Cullis and Hirschler [27] give 3% for volcanoes and approximately 30% each for open-ocean biogenic production, sea spray, and land biogenic production. However, it should be noted that the estimated ranges of natural sources are highly uncertain, mainly because of the extrapolation of a few point measurements to the global scale. Hence, the numbers given vary considerably.

The origin of anthropogenically produced SO$_2$ emissions differs in size between the continents. The approximate regional apportionment of fossil fuel sulfur emissions in 1980 was 16% for China and Japan, 28% for the United States and Canada, 34% for Europe, 15% for the remainder of the northern hemisphere,
and 7% for the southern hemisphere [28]. The main source of the oxidized sulfur from human activity is the burning of coal. The greater part of the world’s coal used for energy burning contains more than 2% sulfur in the form of either pyrite (FeS2) or organic sulfur [6]. In Europe, over half of the SO2 emission in 1996 came from burning of fossil fuels, mostly in power plants [29]. The sector “public power plants cogeneration and district heating” contributes 54% of the total SO2 emission, and 25% is produced by industrial combustion processes [14].

Despite the fact that SO4\(^{2-}\) deposition as well as SO4\(^{2-}\) concentrations in soil solutions and stream waters have been reduced considerably in northwestern Europe and eastern North America [30–34], determination of the source and fate of atmospherically deposited SO4\(^{2-}\) remains a critical issue for scientists and policy makers. Especially in Asia, concern about long-range transport of air pollution and the question of source–receptor calculations are matters of public and political concern between countries [35,36]. In the past, the origin of emissions was usually calculated by long-range transport models that can give only a broad regional perspective. Because stable isotopic values of S can serve as a “fingerprint” to identify S sources and trace their fates in the environment, several studies tried to link isotopic signatures to geographical or chemical origin. Most studies have found striking seasonality between summer and winter \(\delta^{34}S\) values in precipitation in eastern North America with the summer samples being generally depleted in \(^{34}S\) compared with the winter ones [37–40]. These studies concluded that the depleted \(^{34}S\) values in the summer were due to higher emissions of biogenic S that is depleted in \(^{34}S\). Mixing models were used to calculate that the biogenic contribution to the SO4\(^{2-}\) deposition could account for up to 30% of the atmospheric S burden. However, other studies concluded that temperature and solar radiation effects as well as the marine aerosol contribution are responsible for seasonal patterns in \(\delta^{34}S\) and biogenic emissions have been overestimated in the past [41–46]. Because the influence of anthropogenic SO2 emissions on \(\delta^{34}S\) values in precipitation is dependent on the fossil fuel usage of the area, Alewell et al. [46] tried to link stable isotopes to fossil fuel usage of source states in the northeastern United States. However, the high variability of the \(\delta^{34}S\) values of various fossil fuels makes it difficult to use stable S isotopes for identifying whether changing fossil fuel utilization has affected the \(\delta^{34}S\) values in bulk precipitation [46].

As for NOx, the common approach in Europe and North America to reduce SO2 emissions is to define technology, fuel, and pollutant specific emission standards for the most relevant sources. In addition, most countries have limited the allowed sulfur content of fossil fuels. Countries such as Germany, The Netherlands, Italy, and the Nordic countries have limited the sulfur content of heavy fuel oils to 1%, in certain regions even less [15]. In Norway and Sweden, the introduction of a tax on sulfur has resulted in even lower levels. Because sulfur is almost completely oxidized to SO2 during combustion processes, only secondary measures (in this case flue gas cleaning) are relevant for emission reduction. Most
technologies are based on the reaction of SO$_2$ with alkaline agents added as solid or as a suspension of the respective salts [14]. In other techniques, SO$_2$ is oxidized catalytically to SO$_3$, which reacts with water to form sulfuric acid. As for NO$_x$, nontechnical options to reduce SO$_2$ emission (see earlier) have a great potential to reduce emissions at low costs.

3 DEPOSITION PROCESSES AND THEIR MEASUREMENT

3.1 Wet Deposition Versus Dry Deposition

In an open, uniform landscape, bulk deposition (the sum of wet and dry deposition) is measured by simple use of open precipitation collectors. However, this measurement is a fairly accurate estimate only for a homogeneous flat surface. For all other surfaces (e.g., canopies of forests), wet and dry deposition have to be measured separately.

Wet deposition includes particulate diffusophoresis, Brownian diffusion to cloud or raindrops, impact and interception by raindrops, solution and oxidation in droplets, and uptake by falling raindrops [11]. Wet deposition is usually measured by simple use of open precipitation collectors. In a more advanced technique (providing more correct measurements), precipitation collectors will be opened only with the beginning of rain, thus excluding dry deposition during nonrain periods. The latter devices are normally referred to as wet-only samplers.

The deposition of cloud and fog water is sometimes referred to as occult deposition [47,48]. It has been shown that the deposition of cloud and fog water is a considerable part of bulk deposition of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ [49]. Concentrations of major ions in cloud and fog water can be up to 25 times higher than in incident precipitation [49], and this has been suggested as one of the major factors leading to a decline in mountain forests in the Czech Republic and Germany.

Dry deposition leads to direct collection of gases, vapors, and particles on land, plant, and water surfaces. It can be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation [50]. The process of dry deposition involves three steps: turbulent transport from the free atmosphere to a relatively quiescent near-surface layer; boundary layer transport by convection, diffusion, or inertial processes; and chemical or physical capture of the chemical species by the surface [50,51]. The complexity of the individual processes involved and the variety of possible interactions among them already indicate the difficulties in measuring dry deposition. Dry deposition has been estimated to contribute up to half, or even more, of the total sulfur and nitrogen deposition in the northern hemisphere [11,50]. Thus, the need for correct measurement of dry deposition has often been stressed in the past [11,52].

There are no simple, direct measurements for quantifying dry deposition, but measurements can be divided into two categories. The first category, the sur-
face analysis method, examines the chemistry of exposed surfaces such as leaves or surrogate surfaces. This category includes foliar extraction, measurement of throughfall and stem flow (the difference between wet deposition above the canopy and the throughfall measurement below the canopy gives an estimate of dry deposition), cloud droplet collection, watershed mass balance (difference between input with wet deposition and total export yields in dry deposition), isotopic tracers, snow sampling (fresh snow is compared with old surface snow), and aerodynamically designed surrogate surfaces. Each of these methods has its problems. Foliar extractions rely on a large number of representative samples of the investigated surface. This is especially difficult when investigating heterogeneous forests with high canopies. The measurement of throughfall and stem flow in forest ecosystems is a relatively easy to implement, inexpensive method, which gives measurements over long time periods and integrates values measured across the canopy of trees. However, exudation or leaching from plant tissues can change element fluxes considerably, especially for nitrogen, potassium, and protons [53,54].

The watershed-mass-balance approach assumes that the total element input to a watershed is the sum of inputs by wet and dry deposition. Thus, subtraction of wet deposition from the total export from the system would yield dry deposition. However, internal soil pools acting as sinks or sources of elements might often be under- or overestimated by this approach [55,56]. Other surface analysis methods such as snow sampling, aerodynamically designed surrogate surfaces, or isotope tracers all have the problem of being representative for larger scales in space and time [50].

The second category for measuring dry deposition, the atmospheric flux method, infers fluxes from the atmospheric concentrations of the pollutants in question. This includes tower-based Eddy correlation, Eddy correlation from aircraft, Eddy accumulation, gradients method (measurements of contaminant concentration as a function of height), and the variance method (fluctuations in heat flux or humidity to estimate contaminant fluxes) (for detailed descriptions of the methods see Ref. 50).

A simplification of the formula used for the Eddy correlation would be

\[ F = C \times V_d \]

with \( F \) the flux to the surface, \( C \) the atmospheric concentration, and \( V_d \) the deposition velocity.

Deposition velocities vary greatly between gases and as a function of meteorology and the nature of the surface. Thus, in the Eddy correlation measurement, the fluctuation of the vertical wind is measured with a fast-response airflow sensor such as a hot-film anemometer. The fluctuation of the concentration is measured with a sensor for the contaminant of interest. The flux measurements with Eddy correlation pertain to a spatial scale of several hundred meters upwind, with
a zone typically ±15° from the average wind direction [50]. The main advantage of this method is that fluxes can be measured with reasonably high accuracy and good time resolution for ozone, SO$_4^{2-}$, NO, and NO$_2$. The disadvantage of the method is that the technique is accurate only in uniform vegetation with adequate fetch.

In general, atmospheric flux measurements offer certain advantages over surface analysis techniques, mainly that the flux estimates give data over a short period of time and that direct measurement of flux is possible. However, all atmospheric flux measurements require sensor and/or sampling equipment that may be expensive and not always reliable [50]. It is generally agreed that none of the methods in either category is useful for all situations and that a combination of techniques may be needed to maximize the quality of dry deposition data [11,50].

### 3.2 Throughfall Chemistry and Canopy Interactions in Forest Ecosystems

To estimate acid input to the soil in forest ecosystems, there is a need to consider canopy interactions for estimation of the total load to the soil. This includes the measurement of throughfall and stem flow. Throughfall is defined as the water dripping from forest canopies, and the term stem flow describes the water running down the trunks of trees. Nutrient transfer with throughfall and stem flow is usually substantially larger than that in incident precipitation. The alteration of the composition of water in contact with plant tissues may be attributed to both canopy interactions and atmospheric dry deposition. The measurement of throughfall has frequently been used to estimate dry deposition into forest ecosystems. The throughfall method clearly has the advantages of not being restricted to uniform surfaces or adequate fetches (see earlier) while at the same time including all gases and particles deposited at the surface of leaves. Furthermore, it is a fairly easy and inexpensive monitoring method. However, measurement of throughfall has been developed for quantification of element fluxes into forest soils and not for deposition estimates [21]. Physical (particle resuspension, evaporation, passive excretion of ions by diffusion), chemical (ion exchange, erosion of cuticular waxes by ozone or acidity, changes of membrane structure by either SO$_2$, acidity, or ozone), and biological processes (active uptake by higher plant foliage, active excretion by plant tissues, foliar H$_2$S emission, conversions by arthropods, active uptake by lichens and microepiphytes, release of dissolved substances by decomposition) influence the element composition in throughfall [54]. Throughfall fluxes are influenced by diffusion and exchange between the surface water and the underlying apoplast of canopy tissues [21]. Diffusion is the major cause of elevated anionic concentrations in throughfall, and both diffusion and ion exchange contribute to cationic concentrations in throughfall [54]. The rate of canopy exchange is dependent on the el-
elements considered as well as the tree species and ecological parameters. Coniferous trees lose less nutrients in the growing season than deciduous trees [21], but losses continue throughout the dormant season because conifers keep their leaves. Biotic stresses, such as canopy infestation by herbivore insects, can affect throughfall and soil solution chemistry, causing increased concentrations of dissolved organic carbon (DOC) and decreased concentrations of inorganic nitrogen throughout plague situations [57,58]. The amount and timing of precipitation are found to be relevant for canopy leaching: long residence times of the water during fog events or drizzle increase canopy leaching compared with events with large rainfall intensities.

For protons, up to 80% of the proton deposition may already be buffered in the leaves [59,60]. This fraction of deposited acidity reaches the soil not at the soil intersurface with the atmosphere but at the soil intersurface with the roots [60]. Estimation of the actual proton load to the soil is made even more difficult by the proton consumption and production during nitrogen turnover; the effective rate of proton load to soils by acid deposition can be assessed only if the transfer functions of NH$_4^+$ and NO$_3^-$ are known [61]. Nevertheless, due to dry deposition effects, proton deposition with throughfall is in most cases still considerably higher than with wet precipitation only. For a detailed discussion of proton fluxes and concentrations in the rhizosphere, see Chapter 9.

It is beyond the scope of the present chapter to discuss interactions and processes for each element separately. Generally, canopies of the forests increase deposition rates considerably. By considering physical and chemical interactions and processes in the canopy, Matzner [53] gave estimates of wet and total deposition for a spruce and a beech forest ecosystem in the German Solling area at a time of high deposition rates (Table 1).

The generally lower rates in the beech compared with the spruce canopy are due to the loss of leaves (and thus decrease of surface) during the dormant season. The latter is especially obvious for the deposition of protons, where total deposition is twice the amount of wet deposition for the beech forest but four times for

<table>
<thead>
<tr>
<th>Type</th>
<th>H</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>SO$_4^-$</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet deposition</td>
<td>0.8</td>
<td>7.8</td>
<td>3.7</td>
<td>9.8</td>
<td>1.7</td>
<td>0.7</td>
<td>0.4</td>
<td>1.2</td>
<td>23.2</td>
<td>16.7</td>
</tr>
<tr>
<td>Total deposition, beech</td>
<td>2.0</td>
<td>14.1</td>
<td>6.6</td>
<td>17.1</td>
<td>2.9</td>
<td>1.3</td>
<td>0.7</td>
<td>2.1</td>
<td>50.0</td>
<td>32.5</td>
</tr>
<tr>
<td>Total deposition, spruce</td>
<td>3.8</td>
<td>17.0</td>
<td>8.0</td>
<td>21.1</td>
<td>3.9</td>
<td>1.6</td>
<td>0.9</td>
<td>2.5</td>
<td>83.1</td>
<td>38.6</td>
</tr>
</tbody>
</table>

*Source: Adapted from Ref. 53.*
the spruce forest. The same pattern holds true for the deposition of SO$^{2-}_4$, most of which is caused by the dissolution of SO$_2$ in the water films of leaves [53].

Total deposition of nitrogen to forest soils is difficult to measure because deposition is influenced not only by physical and chemical interactions but especially by biological processes. Considerable parts of the deposited nitrogen are assimilated in the canopy by plant leaves or microorganisms. Furthermore, nitrogen species can be converted in the canopy, e.g., from NH$_4^+$ to NO$_3^-$ or N$_{org}$. A rough estimation by Matzner [53] for the Solling area gave canopy uptake of 7 kg N ha$^{-1}$ year$^{-1}$ for beech and 9 kg S ha$^{-1}$ year$^{-1}$ for spruce.

3.3 High Emission Rates Are Not Equivalent to High Deposition Rates

Because of the long-range transport of SO$_2$ and NO$_x$ emissions, the regions or point sources that are the worst polluters do not necessarily receive the highest deposition rates. This phenomenon is frequently discussed and has become a political issue in North America, Europe, and Asia (see also Sec. 5 of this chapter). Although the highest emission rates of SO$_2$ in Europe are measured in central Europe, relatively high deposition rates are spread all over Europe and hit remote areas of northern Europe as well as regions of southern Europe. Highest SO$^{2-}_4$ deposition was measured in the late 1970s and early 1980s, with up to 100 kg S ha$^{-1}$ year$^{-1}$ in the low mountain ranges of Germany and the Czech Republic [32]. A similar situation is found in North America. For instance, the Hubbard Brook Experimental Forest in a remote area of the White Mountains of New Hampshire receives relatively high SO$^{2-}_4$ deposition from the states to the west and south with high emission rates (Illinois, Michigan, New Jersey, New York, Ohio, Pennsylvania, and Wisconsin [46,62]). However, it is noteworthy that deposition rates in North America are generally much lower than in Europe (only up to 17 kg S ha$^{-1}$ year$^{-1}$ [62]).

Because ammonia deposition is much more dependent on nearby point sources, spatial patterns of ammonia deposition normally parallel emission patterns. In Europe, high rates of ammonia emission have been measured generally in central Europe with maximum emission in The Netherlands, Belgium, southeast Germany, Austria, west Hungary, and west France (for maps see Ref. 63). Accordingly, most of central and eastern Europe has high ammonium deposition rates of up to 10 kg NH$_4^+-$N ha$^{-1}$ year$^{-1}$ and The Netherlands, Belgium, southeast Germany, and Austria have up to 20 and in some cases even 30 kg NH$_4^+-$N ha$^{-1}$ year$^{-1}$ [32,63].

4 CONSEQUENCES OF ACID DEPOSITION

The overall consequences of acidic deposition are definitely more than soil and water acidification. A brief discussion of the changes induced in soils and discus-
sion of the effects on forests and biota are given in the following. Other conse-
quences are trace metal mobilization, damage to buildings, and impacts on human
health. For further discussion of soil acidification due to acid rain see Chapter 2.

4.1 Soil Chemical Reactions Induced by Acid Rain

The question of the nature and extent of acidic deposition effects on soils is con-
troversial [64], partly because the effects of acid rain on soils have much in
common with those of acid produced naturally in soils [6, 65]. In general, the fol-
lowing chemical reactions can take place after the deposition process: acid pro-
duction, proton buffering (e.g., cation exchange), precipitation or dissolution of
minerals, ion adsorption or desorption, formation of gaseous compounds, and re-
actions with the biota.

Once deposited, emissions of sulfur dioxide (SO₂), nitrogen oxides (NOₓ),
and ammonia (NH₃) act as acidifying agents in soils and lakes. Several natural
mechanisms (e.g., mineral weathering, deposition of alkaline dust) may neutralize
a certain fraction of the acidifying deposition, depending on the type of the ecosys-
tem and on a range of site-specific conditions (climate, hydrology, etc.). If acid de-
position exceeds this natural absorption capacity, resulting changes in soil and wa-
ter chemistry will cause damage to plants, soil organisms, and aquatic life.
However, the monitoring of soil acidification induced by acid rain is difficult be-
cause of the long time frames involved [66] and the parallel development of nat-
ural acidification processes [65]. Both natural and anthropogenically driven soil
acidification can result in extremely low base saturation, low pH, and low alka-
ilinity [65]. One difference between natural and anthropogenically driven soil acid-
ification is that anthropogenic soil acidification due to acid rain is connected to
high soil solution concentrations of SO₄²⁻ and NO₃⁻ [65]. In contrast, the “acidify-
ing anions” (referring to the anions responsible for proton and aluminum leach-
ing) during natural acidification processes are organic anions and HCO₃⁻.

In parts of northern Europe, forest soil pH has decreased by 0.5 to 1.0 units
during the past 30 to 60 years, at least partly as a result of acidic deposition [67].
The deposition of nitrogen (NH₃, NH₄⁺, NOₓ) in ecosystems may contribute to eu-
trophication and changes in the function and stability of oligotrophic ecosystems
(e.g., heathlands and bogs [67]). High nitrogen and/or SO₄²⁻ deposition has re-
sulted in nitrogen and SO₄²⁻ accumulation in forest soils, leaching of base cations,
and acidification of surface waters. For detailed discussion of element cycling in
the processes of natural and anthropogenic acidification, see Chapter 3.

4.2 The Question of Soil Acidification and Forest Decline

Despite the lack of evidence for direct effects, there appears to be no doubt about
the serious consequences of the complex known as acid rain in central Europe and
northeastern America to forest ecosystems [68, 69] (for a literature overview see
More recently, serious effects of acidic precipitation have been recognized in China, particularly in the new industrial regions such as the Sichuan Province now exploiting extensive nearby coal deposits of high sulfur content [9,70]. However, the timing and magnitude of the forest response to environmental changes depend not only on acidification effects but also on a complex interaction between climate change, accumulation of atmospheric CO₂, and increased global mobilization of nutrients such as N and S [68]. Thus, direct empirical relationships between air pollution and forest decline were statistically hardly significant, even in such large monitoring studies as ICP forests in Europe (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests [71]). However, Erisman et al. [72] attributed the lack of empirical relationships to a combination of the limited comparability of canopy condition data between countries, the large uncertainties in the derivation of environmental stress factors on the local scale, the neglect of several factors influencing canopy condition such as mechanical damage (e.g., wind break, snow break, fire) or biotic stress (insect attacks, fungi diseases, game and grazing, human activities), data availability, and interactions of air pollution with natural stress, age, and other tree characteristics. Furthermore, the relatively short time frame of the ICP forests program (1989 to 1995) did not take into account long-term effects of anthropogenic stress factors and did not allow time to improve methods.

Most countries in central and eastern Europe consider air pollution a serious threat to forest health [69]. During the annual forest survey in the summer of 1998, some 127,000 trees, spread over 5700 sample plots in a network covering most of Europe, were examined for defoliation. Of this number, 24% were assessed as damaged—meaning that they had lost more than 25% of their leaves or needles in comparison with reference trees of the same species [73,74].

In many areas, acid deposition to soils has increased leaching of base cations, leading to deficiency of nutrients, especially Mg and K [67]. Today, many forest soils of central Europe have low base saturation and low pools of exchangeable nutrient cations, especially of Mg [75]. The Mg-deficient nutrition of trees is a widespread phenomenon, estimated to affect up to 57% of the investigated Norway spruce sites in Germany [76]. The appearance of severe deficiency symptoms (yellowing of needles) was related to the exchangeable Mg in the soils and to decreased concentrations of Mg in soil solution [77–79].

Several studies concluded that soil acidification and increased N availability will decrease the fine root mass of trees and shift the rooting zone to upper soil layers or decrease root distribution altogether [67,80,81]. In combination with increased aboveground growth in many areas of Europe, which is most likely due to nitrogen addition, the root/shoot ratio will be decreased. This development will finally cause increase in drought susceptibility and destabilization of trees [81].

Besides loss of nutrient cations, the buffering of protons from deposition causes increased levels of Al in soil solutions that might have detrimental effects.
on tree root growth and nutrient uptake [81,82]. In water culture experiments, the Ca/Al and Mg/Al ratios, rather than the Al concentration itself, largely determined the effect of Al on roots [82–84].

Cronan and Grigal [82] estimated the critical Ca/Al ratio in soil solution to be in the range of 1. Those observed in the Fichtelgebirge mountains (northeastern Bavaria, Germany) decreased to values as low as 0.3 in 1999 [79]. Jorns and Hecht-Buchholz [85] gave a critical value of the Mg/Al ratio in soil solutions as 0.2. The Mg/Al ratios as low as 0.08 have been reported for some German soils [79]. Deficiency of Mg is induced by ion antagonism, especially by high concentrations of H, NH₄, K, Ca, Mn, and Al [83]. Thus, high H and Al concentrations will definitely increase Mg deficiency symptoms. The implication of Ca/Al and Mg/Al ratios for the root activity under field conditions and for mature trees, however, is still debated [86]. Nevertheless, the Ca/Al and Mg/Al ratios are often used as an indicator of detrimental effects of soil acidification on trees and for the calculation of critical loads of acid deposition [86,87].

### 4.3 Acid Rain and Biota in Europe

A review of air pollution effects on European wild species has shown that fungi, mosses, lichens, higher plants, fish, mollusks, amphibians, and mammals are directly or indirectly affected by air pollution [88]. However, with many of the records, it is not possible to attribute the effect noted directly to one particular pollutant [89]. Most records refer to overall acidification effects, although in some regions (central and eastern Europe) acute multipollutant exposure (including heavy metal deposition) is likely to be an additional factor [88]. Some plant species have reportedly increased in numbers because of either enhanced nutrient availability (e.g., increased nitrogen deposition) or changes in community structure (e.g., acid-tolerant grass species are favored [67]). The latter can be caused by either loss of more sensitive species, thus creating a vacant niche, or physical changes in the habitat (e.g., canopy thinning causing increased light on the forest floor). The overall conclusions of Tickle et al. [88] suggest that air pollution and acidification have played a substantial role in population extinction in Europe. However, this conclusion can be applicable mainly to freshwater systems. Rhode et al. [67] have reported no known extinction of plant species in the terrestrial systems, with only the effect on plant biodiversity.

The impacts of acidification on freshwater systems have been well characterized, and it can be concluded that acid deposition reduced alkalinity of lakes and streams [67]. In waters with a low buffering capacity, the pH can be reduced to levels that cause acute and chronic impacts on biological populations. An additional effect on biota is caused by increasing aluminum levels that accompany the lowered pH [67].

So far, most attention on national and international scales has been given to
higher plants, mosses and lichens, and animals rather than fungi, lower plants, or soil biota. Cause–effect relationships between acid deposition and soil biota have been investigated only in case studies. Generally, effects of acid deposition on soil biota are complex (for an overview see Ref. 90). Acid deposition causes species numbers and species diversity of soil fauna to decrease, partly owing to the increase in a few dominant species. Thus, acid deposition may affect competition between soil animals and thereby change the structure of soil animal communities [91]. The change in species composition contributes to a change in forest floor from more mull-like conditions (forest floor type with high biological activity and high turnover rates) to more moder-like conditions (forest floor with medium to low biological activity and turnover rates) [90]. Causal factors for the reaction of the soil fauna to acid deposition are direct sensitivity to protons or other chemical stress associated with acidification (decreased base saturation, reduced availability of cations, increases in aluminum, iron, or heavy metal concentration), change in reproductive success, alteration of the microflora composition, alteration of the chemical contents of leaf litter, changes in microhabitat characteristics (compaction of pore space with a change in forest floor), and shift in competitive relations and/or in predation pressure [90].

Over the next decade, the impacts of acidification and eutrophication in Europe and North America are foreseen to show a decrease, with a consequence of biodiversity showing some recovery. However, a full return to prepollution conditions is not to be expected because of changes in competition patterns and distribution of species. The introduction—whether voluntary or accidental—of species alien to European ecosystems or to other regions of Europe represents an increasing risk, favored by globalization of trade, exchange, and transports [92]. Thus, even if chemical parameters (e.g., nutrient status, acidity) returned to prepollution condition, indigenous species might not be successful in competing with well-established alien species. Furthermore, even while deposition of acidifying substances is declining, the expected growth of economic sectors such as transportation, manufacturing and other industry, recreation, and tourism will put additional stress on many ecosystems. This might prevent ecosystem recovery from acidification effects. Furthermore, genetic transfer between nonnative species, or possibly even genetically modified organisms, and indigenous species, genetic erosion, and isolation of species populations are likely to intensify over the next decade [92]. In summary, European ecosystems are confronted with a change in many environmental factors. Just receding acidification patterns might not help biological systems to recover.

When discussing effects of acid rain on biota, we should not forget that acid deposition can have a negative influence on human health. Increased concentrations of atmospheric S and N species can affect human health either directly (e.g., $SO_2$) or indirectly through ozone formation caused by NOx emissions (see Sec. 2.1.1). In Europe, air pollution episodes of SO2 may have resulted in up to 13,000
additional deaths per year [10]. Furthermore, the acidification of groundwater and drinking water supplies will be a direct human health hazard through high nitrate or metal concentrations (Al, Cd) released from the soils [67]. Furthermore, corrosion damage to drinking water supply systems can cause increased concentrations of Cu in drinking water. Other hazards, such as elevated concentrations of Cd in game or mercury in fish, have also been reported [67].

5 LONG-TERM TRENDS AND FUTURE DEVELOPMENT

This section discusses and presents historical trends, political programs regarding the reduction of anthropogenic deposition, and the deposition rates that can be expected in the future. Because deposition of pollutants is nearly always a sum of a large number of sources, mostly involving different countries [1,56], action to abate air pollution problems has to be coordinated internationally.

5.1 Europe

The hazards of acid deposition, mainly the relation between human health and smoke from coal burning, had already been addressed in the Middle Ages [21]. During periods of low wind speed and/or foggy conditions, the main industrialized cities in Europe experienced high concentrations of smoke, reducing the visibility and increasing the number of deaths each year [4]. From the beginning of the 20th century, emissions of sulfur, nitrogen, and protons showed a steady increase (with setbacks during the world wars and the oil crisis, Fig. 1).

Since the late 1970s and early 1980s, a decreasing trend in the amount of acidifying air pollutants has continued. According to the reports of the European

![Figure 1](image_url)

**Figure 1** Long-term trends in gaseous emissions in Europe. (Data compiled from Refs. 29 and 21.)
Monitoring and Evaluation Programme [63], the total of Europe’s sulfur emissions fell between 1980 and 1993 by more than 45%. By 1997, they were down by 60% [63]. Some countries, such as Austria, Finland, preunification West Germany, Norway, Sweden, and Switzerland, have cut down their sulfur emissions by as much as 75 to 80% between 1980 and 1997. Regarding NO\textsubscript{x} emissions, European countries committed themselves only to ensure that 1994 emissions and beyond would remain below 1987 levels. However, several countries failed even that requirement [93], mostly due to growing prosperity and increased car ownership. Because of the time needed to replace existing vehicles with new ones equipped with catalytic converters, the full effect of these devices has yet to be felt. Still, the total European emissions of nitrogen oxides did fall by 10% between 1987 and 1994 [63]. The emissions of ammonia are estimated to have declined by 18% since 1980 [63].

In the 1980s and 1990s, the achievements in abating nitrogen emissions from stationary sources were almost counterbalanced by increased emissions due to more mobility, despite improvements in motor vehicle technology (for discussion of control techniques see Sec. 2 of this chapter). The European Union (EU) energy consumption is estimated to show a 17% increase from stationary sources and a 37% rise from mobile sources by 2010 [94]. In the agricultural sector, activity levels (livestock, nitrogen fertilizer use) are likely to fall, resulting in lower emissions [92].

The proportion of nitrogen deposited within the country of origin is far greater in the case of ammonia nitrogen than for oxidized nitrogen (see Sec. 2.1.2). Thus, a country will improve its own situation much more efficiently by reducing ammonia emissions [16], and a decrease in NH\textsubscript{3} emissions will be less dependent on international cooperation. This is especially important because differences between countries are distinct (e.g., The Netherlands use predominantly slurry-based systems in livestock production, whereas other countries use far more bedding and straw [16]) and an international abatement strategy is difficult to develop. Furthermore, different abatement strategies have very different efficiency values depending on system characteristics (e.g., climate, soil texture, slopes). Thus, a prediction of ammonia emissions in Europe is difficult to make. Whereas The Netherlands hope to reduce their ammonia emissions from agriculture by at least 50–70%, the overall maximum feasible reduction in Europe without radical agriculture reform is likely to be of the order of 30% [16].

The so-called multieffect protocol of the Convention on Long-Range Transboundary Air Pollution (LRTAP) became effective in December 1999 and was signed by 27 European countries [94]. Provided that the signatories to the protocol actually stick to the ceilings set and that emissions in the nonsignatory countries do not increase, the European emissions of sulfur dioxide, nitrogen oxides, volatile organic compounds, and ammonia may be expected to fall at least to the levels indicated in Table 2.
The sizable emissions of sulfur and nitrogen from international shipping are a matter that has usually been given little attention in Europe. However, emissions from shipping in the northeastern Atlantic and the North and Baltic seas will be equivalent to almost half of the total EU emissions of sulfur and more than a third of those of nitrogen oxides in 2010 [95] (see also Table 3). Use of sulfurous fuels in the shipping sector is not subject to any regulation, with the result that residual oils with a sulfur content of 3–4% are often used at sea [15].

The EU Acidification Strategy is targeting full protection of all ecosystems in the long term. Current interim emission targets for 2010 require reductions of 83% for SO$_2$, 55% for NO$_x$, and 29% for NH$_3$ compared with 1990 levels. However, these levels will not be achieved with existing and proposed policies [92].

When discussing long-term trends of acid inputs in European ecosystems, the “critical loads concept” is noteworthy. The critical loads concept is a first step

<table>
<thead>
<tr>
<th>Location</th>
<th>Sulfur dioxide</th>
<th>Nitrogen oxides</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU</td>
<td>85</td>
<td>49</td>
<td>16</td>
</tr>
<tr>
<td>Non-EU</td>
<td>61</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>Europe</td>
<td>73</td>
<td>36</td>
<td>20</td>
</tr>
</tbody>
</table>

*Emissions from international shipping are not included.

Source: Ref. 94.

TABLE 3  European Emissions of SO$_2$ and NO$_x$ in 1990 and 2010 in Million Tons

<table>
<thead>
<tr>
<th>Source</th>
<th>1990</th>
<th>2010</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO$_2$</td>
<td>NO$_x$</td>
</tr>
<tr>
<td>EU countries</td>
<td>16.3</td>
<td>13.2</td>
</tr>
<tr>
<td>Non-EU countries</td>
<td>21.6</td>
<td>10.2</td>
</tr>
<tr>
<td>International shipping</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Europe, total sum</td>
<td>39.5</td>
<td>25.7</td>
</tr>
</tbody>
</table>

$^a$Projection in the European Commission’s proposed directive for national emission ceilings.

$^b$Projection in the multieffect protocol of the Long Range Transboundary Air Pollution Convention.

Source: Adapted from Ref. 95.
toward an effect-oriented pollution control, bridging the gap between scientists and policy makers [96]. The threshold “below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” is called the critical load [97]. For example, the threshold for terrestrial ecosystems was set by calculating the element concentrations in soil solutions for which no adverse effect on growth of trees and ground vegetation, soil stability, base saturation, and groundwater quality was to be expected [98,99]. For surface waters, indicator organisms were chosen for which the chemical limit is found and entered into mass balance models including all sinks and sources of acidity to estimate the necessary deposition reduction for N, S, and acidity [98].

In an effort coordinated by the UN/ECE Convention on Long-range Transboundary Air Pollution, all European countries estimated the critical loads for their domestic ecosystems. These national estimates were combined into a European critical loads database by the Coordination Center for Effects at the Netherlands Institute for Public Health and the Environment [100]. For the 1999 version of the critical loads databases, the number of countries that submitted the data has increased to 24. National focal centers have selected in total 1,314,806 ecosystems as receptors for calculating and mapping critical loads. Based on the two percentile criteria of the critical loads concept (i.e., the maximum deposition at which 98% of the ecosystems are protected), acid deposition will be greater than the critical loads in 24.7 and 4.3% for the years 1990 and 2010, respectively [1]. The critical loads concept has often been criticized because of its shortfalls (e.g., problems with summarizing geographical data, differences between methods of countries and regions, inflexibility of models not accounting for change over time, difficulties in defining achievable targets, defining clear thresholds, and multipollutant multireceptor problems [96]). However, despite these limitations, the critical loads approach has proved to be a useful practical tool for deriving pollution control strategies [96].

5.2 North America

Comparable to those in Europe, emissions of SO₂ and NOₓ increased continuously in North America since the beginning of the 20th century. Yearly SO₂ emissions in North America had their maximum in the early 1970s, with over 30 million tons per year [21] (see also Fig. 2). Yearly NOₓ emissions peaked in the mid-1980s. Concerns about the phenomena of transboundary flows of acid precipitation and their acidifying effects on ecosystems and hazards to public health led to the establishment of the Long Range Transport of Air Pollutants (LRTAP) program in Canada and the National Atmospheric Deposition Program (NADP) and the National Precipitation Assessment Program (NAPAP) in the United States. The Acid Rain Program of the U.S. Environmental Protection Agency (EPA) resulted in the Clean Air Act of 1995 [101]. Phase 1 of the Clean Air Act required the reduction of SO₂ emission in 1995 by 10 million tons below 1980 levels. The Clean Air Act
affected 445 mostly coal-burning electric utility plants, and the achieved reduction of SO₂ emissions in 1995 was 40% below required levels. A further reduction was required by the year 2000 (phase II). The Act also called for a 2-million-ton reduction in NOₓ emissions by the year 2000 [101]. A significant portion of this reduction was to be achieved by coal-fired utility boilers that would be required to install low-NOₓ-burner technologies.

Although SO₂ emissions are approximately two thirds of those in Europe and NOₓ emissions are about equal, the deposition into the forest ecosystem is only a tenth to a fifth of that measured in European ecosystems. This is due to the different relationship of area and pollution source density in Europe and North America. Highest deposition rates in forest ecosystems in the northeastern United States peaked around 17 kg S ha⁻¹ year⁻¹ in the early 1970s [62,104]. Highest emission rates of SO₂ and NOₓ in North America are found in the east, and especially in the northeast, of the United States [46].

Seasonal variation of SO₄²⁻ deposition is different in Europe and North America because of differences in fossil fuel usage. North America tends to have higher SO₂ emissions in summer due to extensive coal and oil burning to supply electricity for air conditioning, whereas energy for space heating is mainly supplied from natural gas. In Europe, anthropogenic SO₂ emissions are higher in the winter than the summer due to the combustion of fossil fuel for heat in the winter.

5.3 Asia

Northeast Asia is one of the most dynamic and diverse regions of the world. In contrast to North America and Europe, Northeast Asia is only starting to face
emissions problems. Fueled by high population growth and vibrant economies, energy consumption is currently 12% of the world’s total and is projected to increase by a factor of 3 by 2020 [106]. According to Foell et al. [107], a “business-as-usual scenario” would increase the energy consumption in 2020 by about 3.5 times that of 1990. Because fossil fuels will provide much of this energy, emissions of sulfur dioxide are projected to increase by about the same factor (Table 4) [36,105,106]. Unless strong emission control measures are taken, Northeast Asia will face serious problems caused by increasing emissions in the next few decades. The $\text{SO}_4^{2-}$ deposition in 1990 in various regions of China was already at 50 kg S ha$^{-1}$ year$^{-1}$ and reached peaks of 100 kg S ha$^{-1}$ year$^{-1}$ around the cities of Chonqing in Sichuan Province [35]. The situation would already be much more serious were it not for the great quantities of neutralizing dust that are blown in from the desert areas in the west. The use of energy is expected to go on rising, particularly in the power generating and transportation sectors, as a result of booming electrification and a steadily increasing number of private cars [9]. Expected consequences in hard-hit areas (especially South Korea and the Chinese provinces Sichuan and Jiangsu) will be serious damage to crops, natural ecosystems, and human health [9].

Northeast China is the main emitting region (15 million tons SO$_2$ in 1990 [106]), and sulfur is transported across the Korean peninsula to Japan and beyond. However, there are serious efforts to improve the situation. Starting in January 2000, China has followed Japan in trying to improve air quality by making unleaded petrol with low sulfur contents widely available, setting the limits for sulfur in oil to 0.2%, and extending the natural gas network in the country [9].

### Table 4

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Year</th>
<th>Northeast China</th>
<th>Japan</th>
<th>North Korea</th>
<th>South Korea</th>
<th>Asia, total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAU</td>
<td>1990</td>
<td>11.9</td>
<td>0.8</td>
<td>1.7</td>
<td>0.3</td>
<td>34</td>
</tr>
<tr>
<td>BCT</td>
<td>2020</td>
<td>32.5</td>
<td>1.1</td>
<td>5.5</td>
<td>1.4</td>
<td>110</td>
</tr>
<tr>
<td>ACT</td>
<td>2020</td>
<td>22.3</td>
<td>1.0</td>
<td>1.5</td>
<td>0.7</td>
<td>60</td>
</tr>
<tr>
<td>BAT</td>
<td>2020</td>
<td>17.4</td>
<td>1.0</td>
<td>1.5</td>
<td>0.7</td>
<td>NA$^b$</td>
</tr>
</tbody>
</table>

$^a$ BAU, business-as-usual scenario; BCT, basic control technology (modest emission control methods); ACT, advance control (only new point sources install state-of-the-art systems); BAT, best available technology (old and new point sources install state-of-the-art systems).

$^b$ NA, data not available.

*Source: Adapted from Refs. 105 and 107.
Abatement technology for reducing emissions in Asia could cost USD 10 to 30 billion annually by 2030 and still provide only partial protection [95]. The costs for improvement in Northeast Asia according to the various scenarios may appear high, but they cover only technical measures, as do those in Europe and North America. However, there is a great potential for more efficient use of energy, which can reduce emissions at low costs [9]. From the European experience, international cooperation is the most effective means of emission control because of the transboundary movement of air pollutants. Furthermore, there are serious efforts to establish an acid deposition monitoring network in East Asia (participating countries are China, Indonesia, Japan, Republic of Korea, Malaysia, Mongolia, the Philippines, Singapore, Russian Federation, and Thailand).

In summary, acid deposition is evident today in Northeast Asia and will increase dramatically in the future. It is projected that severe damage to ecosystems will occur throughout the region without the introduction of emission controls. There is an urgent need for regional cooperation to improve the level of scientific understanding and develop a basis for region-wide control strategies [36].

5.4 Recovery of Ecosystems after 20 Years of Reduced Deposition in Europe and North America?

Even though deposition has been reduced in large parts of Europe, few signs of environmental recovery can be seen in Europe after 25 years of effort [92]. From a nature conservation viewpoint, Tickle et al. [88] conclude that new European pollution control measures agreed through the United Nations will not be sufficient to avert risk to key ecosystems, especially in countries such as Austria, Belgium, Denmark, Germany, Ireland, The Netherlands, Norway, Switzerland, Sweden, and the United Kingdom. Recovery of soil fauna due to beneficial effects of decreasing acid inputs has been reported only by Boxman et al. [108].

With respect to soil and water acidification, numerous studies in Europe and North America reported widespread aquatic recovery from acidification for European ecosystems due to the significant reduction of anthropogenic sulfate deposition [34,109–111]. However, overall conclusions may be biased because monitoring networks (e.g., ICP-waters in Europe) tend to focus on areas with high sensitivity to acid inputs. The high sensitivity is caused primarily by low storage capacity for sulfate and protons [soils that are characterized by all or a combination of the following parameters: (1) shallow postglacial soil development, (2) sandy soil textures, and (3) a high humus content]. Data for soils with a high storage capacity for sulfate and protons indicate that reversibility of water acidification can be delayed for decades because the release of previously stored sulfate causes cation leaching and acidification of deeper soil layers and waters. Studies from numerous regions of Germany (Solling, Spessart, Frankenwald, Fichtelgebirge, Bayerischer Wald, Schwarzwald) or the Czech Republic reported continu-
ing low pH and low alkalinity in streams or even an increase in groundwater sulfate concentrations [112–117]. In all studies, this delay in recovery was attributed to release of previously stored soil sulfate. Experimental manipulation as well as modeling scenarios with an 80% deposition decrease indicate for all types of soils in Sweden some recovery from acidification effects in the short term, followed, however, by very slow change thereafter [118].

One of the main problems connected to soil and water acidification is the leaching of nutrient cations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\)) from soils. Due to a substantial reduction in particulate emissions within the past 20 years, the nutrient cation concentrations in throughfall and precipitation have declined in some regions. However, nutrient cation concentrations in stream waters did not always decline [113]. The latter is due to continued high SO\(_4^{2-}\) and NO\(_3^-\) concentrations in soil solutions and streams that are accompanied by high cation leaching. Even though high concentrations of nutrient cations in streams were usually interpreted as recovery of waters because of the increase in alkalinity [109,119], they result in a long-term export of nutrients and can point to a continuing (or even increasing) net acidification of soils [77,113]. In this context, it is important to note that an alkalinity increase in streams does not necessarily indicate a reversibility of soil acidification, nor does it indicate biological recovery of the streams so affected.

A significant delay of recovery from acidification in numerous regions of Europe and North America has important implications for water authorities, forest managers, and policy makers. Forest management is still confronted with the need for frequent liming to avoid depletion of soils and subsequent nutrient deficiencies in trees [77]. Water authorities should be aware that for waters (and thus drinking water supply) that drain areas containing soils with a high sorption capacity for sulfate, recovery of aquatic systems will be delayed for decades. Policy makers should consider that nitrogen deposition has to be reduced considerably in order to limit both cation depletion from soils and the further acidification of waters.

6 CONCLUSIONS

Regarding acid rain, industrialized regions of the world show very different trends for future development of sulfur, nitrogen, and proton deposition. Although in Europe as well as North America a significant decrease in sulfur and proton but only a slight decrease in nitrogen deposition can be noted, Northeast Asia is only starting to face the deleterious problems of acid rain. Because of the long-range transboundary transport of emissions of SO\(_2\) and NO\(_x\), international cooperation (in case of the United States, national cooperation between states) has been the only successful way to apply abatement strategies. It can be concluded that reductions in sulfur emissions in North America and Europe were achieved because of available technical options. In contrast, abatement strategies for nitrogen emissions
rely mainly on changes in human behavior (e.g., less motor vehicle use, consuming less meat to reduce livestock numbers) and energy use (e.g., more usage of wind, solar, and water energy; energy-saving strategies). Thus, a decrease in nitrogen emissions has been less successful so far. The good news for ammonia abatement strategies is that countries will directly benefit from their own efforts because there is hardly any long-range transport involved. Thus, there is hope for the future that site- and country-specific abatement strategies will be brought into action without the decades of delay connected with international political cooperation.

Scientific proof of the detrimental effects of acid rain on biota or soils is not easy to give. However, there is plenty of evidence that acid rain causes soil and water acidification, is connected to forest decline, has a negative effect on biodiversity, has a detrimental effect on human health, and can even cause extinction of plant and animal species.

Recovery from the deleterious effects of acid rain after 25 years of decreased sulfur and proton deposition in Europe and North America is up to now reported only for the reversal of chemical trends in aquatic systems. However, biological recovery (recovery of trees, aquatic species, etc.) as well as reversal of soil acidification has been noted to a minor extent only.

REFERENCES
restrial Ecosystems, and Associated Water Bodies. Scope 48. New York: John Wi-
26. MO Andreae, WA Jaeschke. Exchange of sulphur between biosphere and atmo-
sphere over temperate and tropical regions. In: RW Howarth, JWB Stewart, MV
Ivanov, eds. Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems,
27–61.
27. CF Cullis, MM Hirschler. Atmospheric sulphur: natural and man-made sources. At-
of NO\textsubscript{X} and SO\textsubscript{2} from fossil-fuel combustion between 1966 and 1980. Atmos Envi-
30. N Christophersen, A Robson, C Neal, PG Whitehead, B Vigerust, A Henriksen. Ev-
idence for long-term deterioration of streamwater chemistry and soil acidification at
31. AD Newell. Inter-regional comparison of patterns and trends in surface water acid-
32. E Matzner, KJ Meiwes. Long-term development of element fluxes with bulk pre-
cipitation and throughfall in two German forests. J Environ Qual 23:162–166,
1994.
33. GE Likens, CT Driscoll, DC Buso. Long-term effects of acid rain: response and re-
34. CT Driscoll, GE Likens, MR Church. Recovery of surface waters in the northeast-
ern U.S. from decreases in atmospheric deposition of sulfur. Water Air Soil Pollut
35. RL Arndt, GR Carmichael. Long-range transport and deposition of sulfur in Asia.
36. M Yagishita. Establishing an acid deposition network in east Asia. Water Air Soil
37. JO Nriagu, DA Holdway, RD Coker. Biogenic sulfur and the acidity of rainfall in
38. JO Nriagu, RD Coker. Isotopic composition of sulfur in precipitation within the
39. JO Nriagu, RD Coker. Isotopic composition of sulfur in atmospheric precipitation
40. DR Van Stempvoort, JJ Wills, P Fritz. Aboveground vegetation effects on the de-
position and cycling of atmospheric sulfur: chemical and stable isotope evidence.
41. M Novak, SH Bottrell, H Groscheova, F Buzek, J Cerny. Sulphur isotope charac-
teristics of two North Bohemian forest catchments. Water Air Soil Pollut 85:1641–
42. M Novak, SH Bottrell, D Fottova, F Buzek. Temporal and spatial variation in sul-
phur fluxes and $\delta^{34}$S ratios in Central Europe. In: SH Bottrell, ed. GES-IV, Fourth
International Symposium on the Geochemistry of the Earth’s Surface, Ilkley, Eng-


Acid Inputs into Soils from Acid Rain

107. W Foell, C Green, M Amann, S Bhattacharya, G Carmichael, M Chadwick, S Cinderby, T Haugland, J-P Hetteling, L Hordijk, J Kuypers, J Shah, R Shrestha, D
Acid Inputs into Soils from Acid Rain


108. AW Boxman, D Van Dam, HFG Van Dijk, RF Hogervorst, CJ Koopmans. Ecosystem responses to reduced nitrogen and sulphur inputs into two coniferous forest stands in the Netherlands. For Ecol Manage 71:7–30, 1995.


1 INTRODUCTION

Soil acidification is a natural process that is accelerated by agricultural production [1,2]. It has been estimated that 80–90 million hectares of land in the agricultural areas of Australia are acidic, with 30–35 million requiring immediate remedial action \( \text{pH (CaCl}_2 < 4.8 \] [3,4]. In Western Australia alone, two thirds of the soils in the agricultural areas of state are acidic or at risk from soil acidification \( \text{pH (CaCl}_2 < 5 \].

Acid soils can be treated easily and relatively inexpensively using neutralizing agents such as lime (see Chapter 11). However, it is difficult to determine lime rates because acidification occurs slowly, and rates of acidification are hard
These factors, combined with poor awareness of the extent of the problem of acid soils, meant that total use of lime and dolomite in Western Australia was only 117,000 tonnes in 1989–1990 [1]. Despite the extent of acid soils in the state, this had only increased to 177,749 tonnes across 11,300,000 ha of agricultural land under crop or pasture in 1995–1996 [6]. A large research and extension project was initiated in 1996 to increase awareness of soil acidity and liming and to investigate the effects of liming on other components of the production system. A decision aid for estimating net acidification rates (in terms of lime equivalents) for agricultural production systems in Western Australia was produced as part of the project.

This chapter describes the development of the decision aid just mentioned. Although the data presented here specifically apply to the production systems in Western Australia, the approach is valid for any location and production system. Calculated acidification rates using this decision aid are compared with estimates made using soil surveys.

2 QUANTIFYING THE COMPONENTS OF SOIL ACIDIFICATION

The processes that acidify soils [removal of produce (imbalance between cation and anion uptake), accumulation of soil organic matter, leaching of nutrients and fertilizer reactions] are well defined (see Chapters 2 and 3). It can be useful to think of acidification of soils under an agricultural system in terms of the contributions from each of these sources (Fig. 1). Net additions to a “pool” of acid occur when products are harvested, organic matter is accumulated, nitrate derived from the nitrification process in soil is leached, or acidifying fertilizers are applied. An estimate of the amount of acid added to the soil profile of a paddock or field over a year of production can be obtained from the sum of these processes. This in turn can be used to estimate the lime requirements (quantity of lime needed to neutralize the acid added) for different rotations.

We used this approach to estimate the acidification rates of soils in Western Australia under various agricultural rotations. The contribution of each of the major components was determined mathematically and then presented in the form of a simple decision tool for use by farmers and advisers.

2.1 Product Removal

Nutrient cycles are broken when alkaline produce is removed from the original site of nutrient uptake by the plant (see Chapter 2). The amount of acid added to a soil due to product removal is equal to the alkalinity of the produce removed from the system. This can be determined by measurement of the alkalinity of the ash following incineration of the product. Because plants extrude protons during up-
take of cations and extrude alkaline bases or hydroxyl ions in exchange for anions taken up, ash alkalinity can be estimated from the excess of nonnitrogen cations over anions in the product [1,2,7,8]. We estimated the acidification due to product removal in this manner.

A database of the content of all major plant nutrients in over 13,000 samples of seed and other plant parts analyzed from field research conducted in Western Australia was compiled. In combination with published information [9–20], these data were used to determine the average quantities of nutrients in various agricultural products. For animal products (beef, lamb, and wool) the deposition of feces and urine in nonproductive areas, such as stock camps and laneways, was also taken into account. Average concentrations of nutrients in the feces and urine of cattle and sheep and the quantity excreted per day were estimated using a range of sources [21–24]. Twenty-two percent of the excreta from sheep were assumed to be deposited in nonproductive areas of a paddock [25]. This amount was estimated as 0.9% for cattle.

The alkalinity of each product was determined from the difference between the sum of the cations and anions on an equivalent charge basis (charge/atomic weight). This was then expressed in terms of the removal per tonne (for crops) or
per kilogram (for animal products) of produce. This was termed the *product removal number*. The acidification of the soil due to product removal was then calculated by multiplying this value by the quantity of the product that was harvested (Table 1).

### 2.2 Accumulation of Organic Matter

The accumulation of soil organic matter results in the breaking of nutrient cycles and thus contributes to the acidification of soils in a similar manner to the removal of alkaline produce [26]. Because there is little accumulation of organic matter in the old, highly weathered soils that support the extensive agricultural systems of Western Australia [27,28], this component was ignored in our calculations. Future decomposition of organic matter will generally have a liming effect, depending on the nitrogen content and alkalinity of the organic matter [29,30]. Therefore, it was considered that any accumulation of organic matter in the short term would be negated by the liming effect from the decomposition of crop residues in the long term.

### 2.3 Nitrate Leaching

Acid is produced during the formation of nitrate following the complete mineralization of soil organic matter, plant residues, and ammonium-based nitrogen fertilizers. In a complete cycle, this acid is neutralized by organic anions extruded by

---

**TABLE 1** Examples of the Equivalent Acidity Resulting from the Export of Various Agricultural Products

<table>
<thead>
<tr>
<th>Product</th>
<th>Acidity (kmol H⁺ t⁻¹ or kg⁻¹)</th>
<th>Sample yield (t ha⁻¹ or kg ha⁻¹)</th>
<th>Lime equivalent (kg CaCO₃ ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley grain <em>(Hordeum vulgare)</em></td>
<td>0.06</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Canola seed <em>(Brassica napus)</em></td>
<td>0.03</td>
<td>1.3</td>
<td>1.9</td>
</tr>
<tr>
<td>Chickpea seed <em>(Cicer arietinum)</em></td>
<td>0.26</td>
<td>1.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Lupin seed <em>(Lupinus angustifolius)</em></td>
<td>0.3</td>
<td>1.4</td>
<td>21</td>
</tr>
<tr>
<td>Wheat grain <em>(Triticum aestivum)</em></td>
<td>0.05</td>
<td>3</td>
<td>7.5</td>
</tr>
<tr>
<td>Wool (greasy)ᵇ</td>
<td>0.02ᶜ</td>
<td>20ᶜ</td>
<td>20ᶜ</td>
</tr>
</tbody>
</table>

ᵃ Values calculated from the sum of cations minus anions. Examples are also given of the lime requirement to neutralize the acidity for sample yields of each product. These figures were used in the Lime and Nutrient calculator.

ᵇ Includes estimate of removal of excreta to stock camps.

ᶜ Values per Kilogram.
the plant in exchange for nitrate taken up. However, because most of the mineral-
ization occurs within 5 to 10 cm of the surface of the soil [31–34], the topsoil is
acidified if the nitrate is leached to a point lower in the soil profile before it is taken
up by the plant (see Chapter 3). This results in localized acidification, but there is
no net acidification of the soil profile due to the organic anions that are extruded
when the nitrate is taken up by the plant deeper in the soil.

Leaching of nitrate beyond the root zone of the plant results in net acidifi-
cation of the soil. In this case the nitrate is too deep in the soil to be taken up by
plants, so there is a net addition of acid to the profile due to the acid produced dur-
ing the mineralization process. In our calculations we considered only nitrate
leached beyond the root zone as we were calculating the acidification of the entire
soil profile on an area basis.

Few studies have measured the leaching of nitrate under field conditions. In
the past, the contribution of nitrate leaching to acidification has been estimated by
difference using the method of Helyar and Porter [1]. Acidification rates were de-
termined from pH measurements in cleared and uncleared sites [1,5,35–39]. The
contributions to acidification due to the use of acidifying fertilizers and the carbon
cycle components (product removal and accumulation of organic matter) were ob-
tained from farm records, measurements, or the literature [40]. The contribution
of nitrate leaching to acidification was then estimated as the difference between
(1) the product of the measured acidification rates and the pH buffering capacity
of the soil and (2) the sum of the contributions of the other components of acidi-
fication. This method can have large associated errors, particularly with the mea-
surement of pH buffering capacity [27,28,41].

Anderson et al. [42] measured leaching of nitrate from a sandy soil in the
medium- to high-rainfall zone of Western Australia (average rainfall 460 mm per
annum). We used these measurements to estimate the quantity of nitrate leached
per millimeter of annual rainfall under various crops. The estimated quantities of
nitrate leached in each of the rainfall zones of the state were derived by multiply-
ing the quantity of nitrate leached per millimeter by the average rainfall for the
particular zone. This was termed the leaching potential.

The effect of soil texture on nitrate leaching (which was termed the leach-
ing intensity) was estimated on the basis of broad definitions of soil type. Because
Anderson and his colleagues measured nitrate leaching in a sandy soil, a “sand”
was defined as having a leaching intensity (i.e., a multiplication factor) of 1. A
“loam” was defined as having a leaching intensity one half that of a sand, and a
“clay” was assigned a leaching intensity of 0.2 (J.W. Bowden, personal commu-
nication).

The estimated quantity of nitrate leached was determined from the product
of the leaching potential and leaching intensity for all combinations of the three
soil types and four rainfall zones for four categories of crops (Fig. 2). These quan-
tities were comparable with the experiences of local researchers (J. W. Bowden
FIGURE 2  Estimates of the amount of nitrate leached under cereal, oilseed, and legume crops or pastures growing in a “sand,” “loam,” or “clay” soil in the 250 to 325 mm (A), 325 to 450 mm (B), 450 to 750 mm (C), and over 750 mm (D) rainfall zones of Western Australia. Values calculated using the Lime and Nutrient calculator. Note leaching on clay soils in zones (A) and (B) is zero.
and P. J. Dolling, personal communication) and with estimates obtained using a simulation model, the Agricultural Production Systems Simulator (APSIM) [43]. The majority of the nitrate leached from agricultural systems in Western Australia occurs over the summer–autumn period, before winter annual crops are sown, and early in the winter, when crops are just beginning to emerge [44]. The estimated quantity of nitrate leached under cereal crops reflects this asynchrony between demand and supply, particularly with the supply of nitrate derived from soil and residue sources.

It is important to note that for these estimates, the quantity of nitrate leached during the year was apportioned to the current crop. This is not strictly correct because the quantity of nitrate leached depends on both the amount of nitrogen left by the preceding crop (from fertilizer, soil and residue sources) and the nitrogen uptake by the current crop [45]. However, it was used here for simplicity in budgeting.

### 2.4 Acidifying Fertilizers

Fertilizers containing ammonium-based nitrogen compounds or elemental sulfur acidify the soil irrespective of any leaching of nitrate (see Chapter 2). Values for the acidification resulting from these compounds were derived from equations in Tisdale and Nelson [46] and Kennedy [47] (Table 2). The amount of acid added to the soil after application of a particular fertilizer will depend on the type and proportion of compounds that are used in the formulation of the fertilizer. This can be derived from the chemical formulation of the fertilizers, which, in our case, was kindly supplied by the respective fertilizer companies in Western Australia.

#### TABLE 2

<table>
<thead>
<tr>
<th>Fertilizer component</th>
<th>Per kg of nitrogen or sulfur(^b) in fertilizer</th>
<th>Lime required ((\text{kg CaCO}_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate (AS)</td>
<td>1(^{\dagger})</td>
<td>3.6</td>
</tr>
<tr>
<td>Diammonium phosphate (DAP)</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Monoammonium phosphate (MAP)</td>
<td>1</td>
<td>3.6</td>
</tr>
<tr>
<td>Urea</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Calcium ammonium nitrate (CAN)</td>
<td>–0.2</td>
<td>–0.7</td>
</tr>
<tr>
<td>Elemental sulfur</td>
<td>2(^b)</td>
<td>3.1(^b)</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) The quantity of lime required to neutralize the acid produced is also given. Negative values for CAN, which is a mixture of ammonium nitrate and lime, indicate a liming effect from this product.

\(^b\) Values indicated are per kilogram of sulfur.
acidification was expressed per unit of nitrogen (or sulfur), termed the fertilizer number. The acidification resulting from any application of a fertilizer can be determined by simply multiplying the fertilizer number by the amount of nitrogen (or sulfur) applied as that fertilizer.

2.5 The Model

The contribution to soil acidification from the three components described previously was incorporated into a decision support tool, the Lime and Nutrient calculator [48]. The calculator estimates the amount of acid added to the soil (expressed as lime equivalents per hectare) following different rotations. Information about the crop grown, the yield, rainfall, and soil type is entered into the calculator, and an estimate of the total amount of lime equivalents removed per hectare is given by summing the contributions from each component. The calculator was produced both in a printed form, comprising a series of dials, and as a computer spreadsheet. Information on 15 agricultural crops and products was included.

3 ESTIMATING SOIL ACIDIFICATION FOR CROP SEQUENCES

3.1 Calculated Acidification Rates

Sequences of winter annual crops in Western Australia commonly consist of a cereal, typically wheat (*Triticum aestivum*), interspersed with a legume, such as lupin (*Lupinus angustifolius*), and another crop, such as canola (*Brassica napus*). We estimated the acidification rate for such a sequence of crops to illustrate the use of the calculator and the relative importance of the three components described earlier.

In this example, we considered the crop sequence lupin–wheat–canola–wheat grown on a sandy soil in the medium rainfall zone (325 to 450 mm) of Western Australia. The acidification rates were estimated at three levels of productivity, representing average yields and levels 30% above and below that figure (Table 3). The fertilizer rates and mix of fertilizers reflect those likely to be used at each level of productivity.

Predictably, the total acidification rate and average quantity of acid added per year increased with the level of production (Table 3). This increase was attributed to the higher yields (hence greater export of alkaline produce) and, at the highest level of production, to the use of acidifying fertilizers (Fig. 3). In all three cases, leaching of nitrate was the main factor contributing to acidification. This was the same for all levels of production due to the simplified way in which it was estimated by the calculator, but this in part reflects the asynchrony between nitrate supply from mineralization and plant demand.

Tools such as the Lime and Nutrient calculator are particularly useful for ex-
## TABLE 3  Estimated Acidification Rates for a Lupin–Wheat–Canola–Wheat Crop Sequence “Grown” on a Sandy Soil in the Medium Rainfall Zone (325–450 mm) of Western Australia\(^a\)

<table>
<thead>
<tr>
<th>Production</th>
<th>Acidification rate</th>
<th>Crop, grain yield, and N fertilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kmol H(^+) ha(^{-1}) year(^{-1})</td>
<td>Lupin</td>
</tr>
<tr>
<td>Low</td>
<td>7.8 1.9</td>
<td>1.1 t ha(^{-1})</td>
</tr>
<tr>
<td>Moderate</td>
<td>8.0 2.0</td>
<td>1.5 t ha(^{-1})</td>
</tr>
<tr>
<td>High</td>
<td>9.6 2.4</td>
<td>1.9 t ha(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\) Rates were calculated at three levels of productivity (low, moderate, and high) using the Lime and Nutrient calculator. The yields are typical for this environment. Fertilizer applications are appropriate for the levels of production.
amining the likely impact of changes in management on rates of acidification, so-called what if analyses. For example, in the previous calculations, what would be the effect of changing the type of nitrogen fertilizer used? The rates of acidification at the highest level of production were reestimated using three types of fertilizer: DAP (diammonium phosphate), ammonium sulfate, and CAN (calcium ammonium nitrate), which respectively represent moderate, high, and low acidifying fertilizers (Table 4). The rates of each fertilizer were set so that the same amount of nitrogen was supplied in each scenario. The use of ammonium sulfate in place of DAP resulted in a 12% increase in the total estimated acidification over the 4 years. Substituting with CAN resulted in an estimated acidification rate that was 15% lower than that when DAP was used and 24% lower than when ammonium sulfate was used. Naturally, factors such as price, availability, and efficacy will be the major determinants of the choice of fertilizer. However, we suggest that the cost of the acidifying effect of a fertilizer, in terms of the lime required to neutralize this acidification, should be factored into such considerations.

It is important to note that these estimated acidification rates are for the entire soil profile and do not attempt to apportion the acidification to soil layers.
<table>
<thead>
<tr>
<th>Scenario</th>
<th>Crop, yield and N fertilizer application</th>
<th>Acidification rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kmol H⁺ ha⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>Lupin 1.9 t ha⁻¹, Wheat 3 t ha⁻¹, Canola 1.7 t ha⁻¹, 60 kg ha⁻¹ urea, 50 kg ha⁻¹ DAP, DAP 2.5 t ha⁻¹, 60 kg ha⁻¹ urea, 60 kg ha⁻¹ DAP</td>
<td>9.3</td>
</tr>
<tr>
<td>2</td>
<td>Lupin 1.9 t ha⁻¹, Wheat 3 t ha⁻¹, Canola 1.7 t ha⁻¹, 60 kg ha⁻¹ urea, 50 kg ha⁻¹ amm. sulfate, sulfate 2.5 t ha⁻¹, 60 kg ha⁻¹ urea, 50 kg ha⁻¹ amm. sulfate</td>
<td>10.4</td>
</tr>
<tr>
<td>3</td>
<td>Lupin 1.9 t ha⁻¹, Wheat 3 t ha⁻¹, Canola 1.7 t ha⁻¹, 60 kg ha⁻¹ urea, 40 kg ha⁻¹ CAN, CAN 2.5 t ha⁻¹, 60 kg ha⁻¹ urea, 40 kg ha⁻¹ CAN</td>
<td>7.9</td>
</tr>
</tbody>
</table>

*Rates were calculated using the Lime and Nutrient calculator for three fertilizer scenarios that supplied the same quantity of nitrogen.*
Acidification due to the leaching of nitrate and acidifying fertilizers will tend to occur in the topsoil, where the nitrification process occurs. In contrast, acidification resulting from the removal of alkaline produce, due to imbalance of cation and anion uptake, will tend to acidify the soil deeper in the profile (see Chapter 3). This is particularly true for legume species [28,35,49].

3.2 Comparing Predicted and Measured Values

Acidification rates under agricultural production systems in Western Australia have been determined from soil surveys [27,28,35,41]. In these studies acidification rates were estimated on the basis of the difference in soil pH between cleared and uncleared sites, using the formula developed by Helyar and Porter [1]. We compared these results with estimates made using the calculator (Table 5).

In all cases the calculator gave results that were higher than those estimated from the soil surveys. The contributions to acidification from the removal of alkaline produce (C cycle) were similar between the two estimates; however, the contribution from N cycle components (nitrate leaching and acidifying fertilizers) were higher using the calculator, by a factor of 2 on loam soils and a factor of 5–10 on sands.

Measured rates of nitrate leaching under agricultural systems in Western Australia are far higher than those that were previously estimated by difference [42]. These measurements, which were determined on deep, sandy soils in a medium- to high-rainfall zone, are at the upper end of leaching rates in this environment. However, they indicate the potential for nitrate to be leached. In addi-

<table>
<thead>
<tr>
<th>Rotation</th>
<th>Soil type</th>
<th>N cycle</th>
<th>C cycle</th>
<th>Total</th>
<th>N cycle</th>
<th>C cycle</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>LWLWLW</td>
<td>Yellow sand</td>
<td>0.22</td>
<td>0.2</td>
<td>0.42</td>
<td>1.8</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>PPPWPPPW</td>
<td>Yellow sand</td>
<td>-0.13</td>
<td>0.34</td>
<td>0.21</td>
<td>1.3</td>
<td>0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>PPPPPWLWW</td>
<td>Sandy duplex</td>
<td>-0.18</td>
<td>0.33</td>
<td>0.15</td>
<td>1.4</td>
<td>0.3</td>
<td>1.7</td>
</tr>
<tr>
<td>WWWWVVVV</td>
<td>Loamy sand</td>
<td>0.34</td>
<td>0.01</td>
<td>0.35</td>
<td>0.54</td>
<td>0.06</td>
<td>0.6</td>
</tr>
<tr>
<td>PWPWPWP</td>
<td>Loamy sand</td>
<td>0.08</td>
<td>0.33</td>
<td>0.41</td>
<td>0.4</td>
<td>0.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

a Rates are divided into nitrogen cycle (nitrate leaching and nitrogen fertilizer) and carbon cycle (product removal) components.

b L, lupin (Lupinus angustifolius); W, wheat (Triticum aestivum); P, annual pasture (subterranean clover-based, Trifolium subterraneum).
tion, they highlight the importance of the asynchrony between supply of nitrate from mineralization and demand for mineral nitrogen by plants, which is a feature of many annual production systems throughout the world.

Dolling and Porter [27] stated that “the acidification rate and mechanisms in this study can only be taken as a guide as there are many potential sources of error,” particularly pH buffering capacity. Recent work by Tang and colleagues [50] has highlighted the range of values of pH buffering capacity that are obtained using different laboratory techniques. They found that acidification rates calculated using pH buffering capacity accounted for only 59 to 65% of those measured in a pot experiment. In addition, acidification rates estimated from soil surveys assume that the soil acidification in uncleared areas is negligible, whereas even these “natural” ecosystems usually acidify with time [1].

3.3 Planning for Sustainable Production

Calculations such as those used in the preceding examples are useful to provide an estimate of the rate of acidification of a particular crop sequence. This information is an important first step in determining what applications of lime are required to maintain productivity. However, these calculations cannot be used in isolation. Estimated acidification rates need to be considered in conjunction with the results of soil pH tests and the sensitivity to acidity of the species being grown in order to ascertain whether neutralizing agents need to be applied to raise, or merely to maintain, soil pH. In combination, these pieces of information will allow farmers to make better informed decisions regarding the applications of liming agents to their paddocks or fields.

Estimates of acidification rates based on the contributions of the major components are helpful in identifying which aspects of agricultural systems could be altered to reduce rates of acidification. For example, is it possible to use a less acidifying fertilizer? What changes can be made to the system of production to reduce the leaching of nitrate [43,51–61]? These questions are critical as we develop agricultural systems that are better suited to the vagaries of an environment and are able to progress toward sustainable production of essential food and fiber.

4 CONCLUSIONS

The method used in this chapter to calculate acidification rates can be applied to agricultural production systems anywhere in the world. Estimates are obtained for the four main causes of soil acidification; removal of alkaline produce, accumulation of soil organic matter, leaching of nitrate, and use of acidifying fertilizers, using local data.

The ash alkalinity of harvested produce can be measured in a laboratory or calculated from chemical analyses of the product in question. Similarly, estimates
of the accumulation of soil organic matter and the composition of residues can be used to estimate these “removals” from the system. The acidifying effect of nitrogen and sulfur compounds used in manufactured fertilizers is well documented, so this component can be determined for any fertilizer based on its formulation. The acidification resulting from the leaching of nitrate produced in situ is the most difficult component to estimate. However, estimates will be made more easily as more measurements of the leaching of nitrate are being made worldwide because of recognition of the need to better manage inputs to help to control effects such as acidification and the eutrophication of waterways.

ACKNOWLEDGMENTS

We would like to thank the many people from the Centre for Legumes in Mediterranean Agriculture, Department of Agriculture Western Australia, Chemistry Centre (WA), The University of Western Australia, TopCrop West, and CSIRO who helped with the development and evaluation of this calculator. We also thank staff from Wesfarmers CSBP, RTC Agribusiness, Elders Ltd., Wesfarmers Dalgety, Summit Fertilisers, United Farmers, Kondinin Group, and the numerous private agricultural consultants who provided valuable feedback. The cooperative development of the Lime and Nutrient calculator was supported by the Grains Research and Development Corporation, with additional assistance from Wesfarmers CSBP and RTC Agribusiness.

REFERENCES

7. SC Jarvis, AD Robson. The effects of nitrogen nutrition of plants on the development of acidity in Western Australian soils. II Effects of differences in cation/anion balance...
Modeling Acidification Processes in Agricultural Systems

Kirsten Verburg
CSIRO Land and Water and APSRU, Canberra, Australia

Jörg Braschkat
CSIRO Plant Industry, Canberra, Australia

Zvi Hochman
CSIRO Sustainable Ecosystems and APSRU, Toowoomba, Australia

Andrew D. Moore
CSIRO Plant Industry, Canberra, Australia

Keith R. Helyar
Agricultural Research Institute, NSW Agriculture, Wagga Wagga, Australia

Mervyn E. Probert
CSIRO Sustainable Ecosystems and APSRU, Indooroopilly, Australia

John N. G. Hargreaves
CSIRO Sustainable Ecosystems and APSRU, Toowoomba, Australia

Richard J. Simpson
CSIRO Plant Industry, Canberra, Australia
1 INTRODUCTION

Soil acidity increasingly limits production in agricultural systems in many parts of the world. Whereas in some cases the acidity is naturally occurring, in many others agricultural practices have accelerated soil acidification. A range of management practices has been proposed to control and ameliorate soil acidification. Liming has undoubtedly received most attention, but other options that have been suggested include the application of alternative ameliorants as well as modification of the production system through changes in crops grown, fertilizer, or residue management (see Chapters 12 and 13). Laboratory tests and field trials have assessed the effectiveness of many of these practices in increasing pH and reducing aluminum activity. Results have, however, often been variable. This is probably due to interactions with other processes operating in the system as well as the influence of weather and soil variability. Simulation models can be used to address these issues by integrating and extrapolating experimental observations. In this chapter we describe how incorporation of a proton budget framework into two models of agricultural systems provides us with tools to analyze soil acidification as a function of soil, climate, and agricultural management.

2 SOIL ACIDIFICATION: RELEVANT CONCEPTS

The processes involved in soil acidification have been described by, among others, van Breemen et al. [1], de Vries and Breeuwsma [2], Binkley and Richter [3], Helyar and Porter [4], and also by Bolan and Hedley (Chapter 2). As outlined by these authors, the various processes can be grouped according to the element cycle to which they belong. Table 1, for example, lists the main proton-producing and proton-consuming processes of the nitrogen cycle. The processes can also be presented in the form of diagrams [1–5]. Figure 1 is an example of such a diagram for the nitrogen cycle. From this, it was realized that in order to calculate the proton budget for processes associated with the nitrogen cycle, one needs only to keep track of changes in nitrate and ammonium. A reaction causing an increase in ammonium always leads to consumption of protons, whereas a decrease in ammonium leads to production of protons. The opposite happens for increases and decreases in nitrate. For example, mineralization of organic matter consumes one proton for every ammonium ion produced (reaction 2a), and nitrification leads to the production of two protons for every ammonium ion converted to nitrate (reaction 3). Similar diagrams can be drawn for the other element cycles. In these cycles, too, it is often necessary only to keep track of a few compounds.

The finding that only a few compounds need to be tracked led Helyar and Porter [4] to develop a proton budget framework based on three product pools: reference state, alkaline, and acid products (Fig. 2). In this framework, additions, losses, and accumulation of compounds in the alkaline or acid pools are associ-
<table>
<thead>
<tr>
<th>Process left to right(^a)</th>
<th>Process right to left</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Urea hydrolysis ((\text{NH}_2)_2\text{CO} + \text{H}_2\text{O} + 2\text{H}^+)</td>
<td>(\rightarrow) (2\text{NH}_4^+ + \text{CO}_2)</td>
</tr>
<tr>
<td>(2a) Mineralization of organic N (\text{RNH}_2 + \text{H}_2\text{O} + \text{H}^+)</td>
<td>(\leftrightarrow) (\text{ROH} + \text{NH}_4^+)</td>
</tr>
<tr>
<td>(2b) NH(_4)(^+) immobilization</td>
<td></td>
</tr>
<tr>
<td>(3) Nitrification (\text{NH}_4^+ + 2\text{O}_2)</td>
<td>(\rightarrow) (\text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O})</td>
</tr>
<tr>
<td>(4) Denitrification (5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+)</td>
<td>(\rightarrow) (2\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O})</td>
</tr>
<tr>
<td>(5) NO(_3) immobilization (\text{ROH} + \text{NO}_3^- + \text{H}^+ + 2\text{CH}_2\text{O})</td>
<td>(\rightarrow) (\text{RNH}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O})</td>
</tr>
<tr>
<td>(6) NH(_3) volatilization (\text{NH}_4^+)</td>
<td>(\rightarrow) (\text{NH}_3 + \text{H}^+)</td>
</tr>
<tr>
<td>(7) Uptake of NH(_4)(^+) (\text{ROH(plant)} + \text{NH}_4^+)</td>
<td>(\rightarrow) (\text{RNH}_3(\text{plant}) + \text{H}_2\text{O} + \text{H}^+)</td>
</tr>
<tr>
<td>(8) Uptake of NO(_3) (\text{ROH(plant)} + \text{NO}_3^- + \text{H}^+ + 2\text{CH}_2\text{O})</td>
<td>(\rightarrow) (\text{RNH}_3(\text{plant}) + 2\text{CO}_2 + 2\text{H}_2\text{O})</td>
</tr>
</tbody>
</table>

\(^a\)Numbers refer to the schematic presentation in Fig. 1

Adapted from: Ref. 2.
**FIGURE 1** Schematic presentation of the proton-producing (+H⁺) and proton-consuming (−H⁺) reactions in the nitrogen cycle; numbers refer to the reactions listed in Table 1.

**FIGURE 2** Three product pools for determining acid production by the nitrogen cycle. (Adapted from Ref. 4.)
ated with the net production or consumption of protons. Additions, losses, and accumulation of products in the reference state are considered neutral, as are transformations between products within this pool. For practical purposes the reference state is defined so that the measurements required to establish the proton budget are as simple and practical as possible. For the nitrogen cycle, for example, only measurements of nitrate and ammonium fluxes and accumulation are required to calculate the net effects on acidification of all the reactions in Fig. 1. Ammonium is considered an alkaline product, meaning that its addition is counted as proton producing (acid) and its accumulation and its loss are counted as proton consuming (alkaline). Nitrate, on the other hand, is considered an acid product, with addition being equivalent to consuming protons (alkaline) and accumulation and loss equivalent to producing protons (acid). Note that the additions and losses do not themselves involve production or consumption of protons, but the net effect of these processes relative to the reference state does. For example, loss of nitrate through leaching is not acidifying in itself but only following mineralization and nitrification of organic nitrogen: mineralization to ammonium consumes one proton, nitrification produces two protons, so that the net effect is a production of one proton for every nitrate ion accumulated or leached.

Similar pools were defined for the carbon cycle, leading to a net acid addition equation:

\[
\text{Net acid addition} = (\text{carbon cycle effects}) + (\text{nitrogen cycle effects}) - (\text{addition of other alkalis}) + (\text{net addition of acids})
\]

\[
= (O_{Ac} - O_{Acc} + HCO_{3ac} + HCO_{3ex} - HCO_{3ad})
+ (NH_{4ad} - NO_{3ad} - NH_{4ac} + NO_{3ac} - NH_{4ex} + NO_{3ex})
- (L_{ad}) + (H_{ad}) - (H_{ex})
\]

where the units of net acid addition are mol H\(^+\) ha\(^{-1}\) period\(^{-1}\) and ac stands for accumulation, ex for loss, and ad for addition. OA represents the organic anions in organic matter, residues, and removed plant products; HCO\(_3\) represents the bicarbonate products in solution; and L represents lime or other alkali additions. Helyar and Porter [4] give a detailed description of the various terms and how they are measured or estimated.

Because the Helyar and Porter model considers acid production and consumption relative to the reference state, Eq. (1) needs to be used with care. For example, addition of an ammonium fertilizer (NH\(_{4ad}\)) is considered acid although it does not lead to acidification if it remains as ammonium in the soil. Ammonium accumulation (NH\(_{4ac}\)) is calculated as alkaline, so the two terms balance each
other out. Similarly, nitrate leaching (NO$_{3ex}$) is calculated as acid but in itself does not lead to acidification as it leads to a reduction in accumulated nitrate (NO$_{3ac}$), a term that is accounted as alkaline. Denitrification, an alkaline process whereby nitrogen is lost as one of the gases N$_2$, N$_2$O, or NO, which are all in the reference state, is represented as a reduction in accumulated nitrate (NO$_{3ac}$).

Not all proton-producing and proton-consuming reactions are represented in Eq. (1). In particular, those relating to buffering of soil pH (cation exchange, weathering) are not included. These are the inorganic reactions that occur in the soil in response to the addition of acids or alkalis. A full budget is, therefore, not calculated. Instead, the Helyar and Porter framework combines Eq. (1) with an equation describing the change in pH over a given period as a function of net acid addition during that period and the soil pH buffer capacity (pHBC):

$$\text{pH change} = \frac{\text{net acid addition}}{\text{pHBC} \times W}$$

where the pH buffer capacity is defined as mol H$^+$ kg$^{-1}$ (pH unit)$^{-1}$, and W is the weight of the component of the ecosystem to which the pH buffer capacity applies (kg ha$^{-1}$).

The Helyar and Porter framework has been used in several Australian studies to determine the main factors causing accelerated acidification in soils under agriculture. Within the carbon cycle, these were found to be accumulation of organic anions in soil organic matter and removal of organic anions in products or their transfer in animal excreta to stock camps [4,6–11]. Within the nitrogen cycle, the single most acidifying cause was the leaching of nitrate following nitrification of ammonium, which was either applied as fertilizer or mineralized from organic nitrogen [12,13].

In most studies the model has been used in a retrospective mode because an estimate of the nitrate leaching term (NO$_{3ex}$) was unavailable. Long-term data on the change in soil pH were obtained from historical records or samples (e.g., [11]) or derived from fenceline comparisons (e.g., [12–14]) and combined with pH buffer capacity data to calculate the net acid addition over the period studied. By equating Eqs. (1) and (2) when both were arranged to estimate net acid addition, the nitrate leaching term was obtained by difference. Other terms in Eq. (1) were either calculated from measurements or from historical records or were assumed to be negligible (HCO$_{3ac}$, NH$_{4ac}$, NO$_{3ac}$, NH$_{4ex}$). This approach effectively assumes that all acidification that cannot be accounted for by other processes is due to nitrification of ammonium followed by nitrate leaching with a strong alkali cation [15]. Unfortunately, this can lead to large uncertainties or even erroneous results. Dolling and Porter [8] and Dolling et al. [9], for example, arrived at negative values (suggesting an alkaline effect) for the NO$_{3ex}$ term, which is supposed to be acidifying. It indicates that the error in their calculations was at least of the same magnitude as the nitrate leaching term. Uncertainty in the nitrate leaching
term is probably also why estimates of the relative contributions of carbon and nitrogen cycles to acidification have been highly variable (e.g., [6,7,16]).

The pH buffer capacity can be an important source of error in the application of the Helyar and Porter framework. Changes in pH buffer capacity over time are usually ignored due to lack of data. This can lead to under- or overpredictions of proton production, especially in situations where the levels of organic matter changed dramatically over the period of study. In addition, slow buffering reactions such as dissolution of aluminosilicate minerals are often not included when the pH buffer capacity is measured using a short period of reaction. This leads to underestimation of proton production by Eq. (2) [14]. Furthermore, Porter et al. [15] emphasize that organic anion accumulation in soil organic matter and organic anion export to stock camps are calculated using conversion factors of questionable accuracy. All these factors increase the uncertainty in the nitrate leaching term when the model is used in a retrospective mode with nitrate leaching loss being estimated from the unaccounted component of acid addition. It is noted that Moody and Aitken [12] point out that processes such as denitrification, volatilization, and leaching of organic acids with subsequent deprotonation are ignored, but this is not a problem because effects on the proton budget of losses of carbon or nitrogen in the reference state are taken into account by the accounting system.

Despite these limitations, the framework has been useful for discerning the main causes of soil acidification in various agricultural systems and for identifying possible strategies for reducing soil acidification. Moody and Aitken [12], for example, performed sample calculations to analyze the potential effect of changes in management practices under bananas, and Ridley et al. [6] made suggestions for improved pasture management based on an analysis of carbon cycle acidification. Similarly, application of the framework to two Leucaena-based pastures in different locations (humid subtropical environment vs. semiarid tropics) has highlighted the effect of climate on some of the acid balance terms ([11], A.D. Noble and R.J. Jones, CSIRO Land and Water and CSIRO Tropical Agriculture, Townsville, personal communication, 1997).

Two studies applied the Helyar and Porter model in prospective mode. Ridley et al. [16] and Poss et al. [17] calculated nitrate leaching by combining drainage data with measured nitrate concentrations in deep soil water or drainage water. While allowing a direct assessment of the effect of nitrate leaching on acidification, the proton budget calculations are in this case restricted to the limited length of such detailed field experiments. Calculated pH changes could, therefore, not be verified as they were of the same order as seasonal variability in soil pH [16].

Several studies have shown that the rate of acidification or pH change within the soil profile is not uniform with depth (e.g., [17–20]). Similarly, the pH buffer capacity is not constant with depth (e.g., [14,21]). In the application of the Helyar and Porter framework, Eq. (2) is therefore applied to the individual soil sampling depth intervals, and a total acid increment for the profile is obtained by
summing these acid inputs. Despite recognition of the differential rate of acidification within the profile, however, most studies persist in applying Eq. (1) of the Helyar and Porter framework to the profile as a whole. Especially in cases where acidification occurs in the topsoil while alkalinization occurs in the subsoil or vice versa, this bulk assessment could fail to recognize the importance of the various processes contributing to development of pH profiles. When Poss et al. [17] applied the Helyar and Porter framework separately to topsoil and subsoil, they found little acidification of the profile as a whole, corresponding to little nitrate leaching out of the root zone. There was, however, significant movement of nitrate within the profile, resulting in acidification of topsoil due to nitrification there and alkalinization of subsoil following uptake of nitrate by plant roots. An analysis of acidification at the soil layer level is therefore useful and might help identify or improve management strategies aimed at ameliorating topsoil or subsoil acidification.

In this context, the transport of acidity and alkalinity within the profile is important as well. An earlier multilayer implementation of the Helyar and Porter framework, the SPAM model (Soil Profile Acidification Model [22,23]), partly addressed this issue. It used a net acidification rate of the profile as a whole derived from Eq. 2 and distributed this acidity on the basis of movement of alkalis and acids within the profile and ion intake balances for the roots in each layer. Nitrate absorption patterns were obtained by fitting against actual pH data. Although retrospective, the model proved useful in the analysis of profile acidity development.

The uncertainty in nitrate leaching, the transport of acidity within the profile, and the need to analyze soil layers separately are issues that can all be addressed if the Helyar and Porter framework is combined with a model that simulates the underlying carbon and nitrogen cycle processes (including nitrate leaching) and ion uptake and excretion in each layer. Two Australian agricultural systems models, GRAZPLAN [24] and APSIM (Agricultural Production Systems Simulator [25]), are particularly suited to linkage with the proton budget calculations. These models predict, at the soil layer level, all the major transformations and fluxes of carbon and nitrogen that contribute to soil acidification. For example, in APSIM the soil residue module simulates decomposition of residues and the effect of various tillage practices, and the soil nitrogen module describes urea hydrolysis, mineralization, immobilization, nitrification, and denitrification [26]. Uptake of nitrogen is part of the crop modules, and transport and leaching of nitrogen are simulated by the water balance modules Soilwat [26] or SWIM (Soil Water Infiltration Movement [27]). Because both GRAZPLAN and APSIM predict nitrate leaching, development of a soil acidification module in these agricultural systems models allows not only quantification of soil acidification but also, in contrast to the retrospective use of the Helyar and Porter framework, prediction of changes in pH.

Another advantage of implementing the proton balance calculations within these agricultural systems models is that it provides the ability to conduct
simulations using long-term weather data sets. These simulations can be used to explore experimental outcomes or to predict the impacts of weather and management on soil pH change (so-called what-if scenarios). Extrapolation of experimental results to other soil types or weather conditions is also possible. Modeling thus provides opportunities for analyzing the effect of different management options aimed at reducing or ameliorating soil acidification.

The Helyar and Porter proton budget calculations have been implemented in both APSIM and GRAZPLAN. These developments (APSIM-SoilpH and the GRAZPLAN soil acidity model) have been largely independent because of the history and different focus of the models: GRAZPLAN deals with grazing enterprises, whereas APSIM is mainly concerned with cropping systems. In this chapter we describe how the proton budget equations have been implemented in the two models, discuss some of the difficulties of capturing complex and interacting processes in models, and give illustrations of model usage. Both acidification models are currently undergoing testing. Results presented here are, therefore, preliminary. Nevertheless, we hope that the examples give an idea of the opportunities that are provided by modeling of acidification processes as well as presenting an understanding of some critical aspects such as parameterization requirements and model limitations.

In the next section we first provide relevant background details of the “parent” models GRAZPLAN and APSIM before describing their acidification modules. These descriptions are followed by examples from both models, and we conclude the chapter with some remarks on opportunities and limitations of model usage and plans for further developments.

3 GRAZPLAN AND APSIM: TWO AGRICULTURAL SYSTEMS MODELS

Models are powerful tools in many fields of research, development, and management. Two models that in recent years have contributed to Australian agricultural systems management and research are GRAZPLAN and APSIM. GRAZPLAN is a suite of decision support tools aimed at helping farmers manage grazing enterprises. It is being developed by scientists at CSIRO Plant Industry. APSIM was originally designed as a tool for systems research, allowing a combination of different soil, crop, and pasture models to simulate soil and crop management dynamically using conditional rules. It has, however, also been used in extension activities to assist farmers in managing crops and croplands. APSIM is being developed by the Agricultural Production Systems Research Unit (APSRU), a collaboration between the CSIRO Divisions of Sustainable Ecosystems (CSE) and Land and Water (CLW) and the Queensland Department of Primary Industries (QPI) and Natural Resources and Mines (DNRM).
3.1 GRAZPLAN*

Publicly available decision support tools included in the GRAZPLAN suite are MetAccess for analysis of weather data [24], LambAlive for lamb mortality [24], GrazFeed for feeding tactics [28], and GrassGro [29] for pasture and animal production. Embedded in these decision support tools are dynamic simulation models that describe certain aspects of the system, e.g., pasture growth, soil moisture, and animal biology. The most recent development within GRAZPLAN is NutriAce (Fig. 3). It is available as a prototype and capable of simulating the cycling of carbon, nitrogen, phosphorus, and sulfur in the grazed pasture systems of temperate Australia. The soil acidity model is part of this development.

Simulations in NutriAce are run on a daily time step, with the user specifying initial conditions and parameter values that describe the specific location, the pasture, and the animal enterprise being simulated. NutriAce uses weather data held in MetAccess weather files [24]. Pasture and sheep or beef enterprises are simulated using the pasture and animal models from the GrassGro decision sup-


![Figure 3](https://example.com/nutriace.png)

**Figure 3** Structure of NutriAce.
port tool [28,29]. These models have been extended to include cycling of nitrogen, phosphorus, and sulfur. Pasture may comprise a mixture of plant species. This is particularly important because nitrogen inputs to many Australian grazing systems are mainly through nitrogen fixation by pasture legumes. The soil water model is also an adaptation of that used in GrassGro. The soil nutrient component of NutriAce is a further development of the soil nutrient cycling component of the McCaskill-Blair model [30–32].

The GRAZPLAN decision support tools MetAccess, GrassGro, and Grazfeed are already successfully used by consultants, rural advisers, and graziers in a diverse range of activities, from drought feeding strategies and optimizing lambing time to fodder reserve policies and decisions on various grazing management options [33–35]. NutriAce was designed to help graziers develop longer term fertilizer strategies. Testing of the prototype version of NutriAce has demonstrated that there is a range of production issues to which the model can be applied and that plausible simulations of pasture systems can be made.

Although developed as decision support tools for farmers and their advisors, the different components of GRAZPLAN have also been used in systems research. Donnelly et al. [36], for example, used GrassGro to evaluate criteria for the definition of exceptional drought, Cayley et al. [37] used it to compare spring and autumn lambing options, and Hill et al. [38] used GRAZPLAN in combination with satellite data to describe spatial variability in pasture growth at a farm scale. An example of model use in economic analysis is that of Scott and Cacho [39], who used production figures from GrassGro simulations to underpin a long-term investment analysis of fertilizer policies.

3.2 APSIM*

The APSIM framework has a modular structure in which crops and major soil processes are dealt with in separate modules (Fig. 4). These modules can be plugged into and out of the system as required. Thus, it allows the choice of a configuration of modules that best reflects the system to be simulated. Another feature of the model is that the soil provides a central focus; crops, seasons, and managers come and go, finding the soil in one state and leaving it in another [25]. Currently there are 25 crop or pasture modules, 10 soil and related modules, and a number of program management and control modules. Communication is via the central engine, with all active modules called once a day in a user-specified order.

The user has a choice of two water balance modules: SoilWat, a tipping bucket module, or SWIM, which is based on a numerical solution of the Richards equation. Dynamics of soil organic matter are dealt with by the SoilN module and decomposition of surface residues in the Residue module. Multiple crop modules

* For more information, visit the web site: http://apsim-help.tag.csiro.au/
can be active at any time, with APSIM handling intercropping issues such as competition for light, water, and nitrogen. A powerful module in the simulation of many scenarios is the Manager module. It provides a user-defined, flexible, and rule-based management system that permits a simulation to mimic realistically both natural and interventionist actions within the system (e.g., to sow on a specified criterion based on rainfall and soil water). Field operations such as sowing, irrigation, or tillage are executed in response to calls to the operations module or activated by statements in the manager logic.

APSIM’s performance in relation to specific modules has been reported in a number of studies (e.g., Wheat [40]; Lucerne [41]; Sugar [42]; SoilWat, SoilN, and Residue [26]). Various APSIM configurations have been tested against experimental data and subsequently used with historical weather records to analyze temporal variability and explore soil and crop management scenarios. For example, a configuration including Wheat and SoilWat was used by Asseng et al. [43] to simulate yield, deep drainage, and nitrate leaching for a deep sand in Western Australia and study the effect of split applications of nitrogen fertilizer. Management of nitrogen fertilizer was also the focus of studies by Keating et al. [44] and Verburg et al. [45], who looked at the impact of irrigation management and soil fertility on nitrate leaching under sugarcane using a configuration based on SWIM and Sugarcane. Impact of management of legume–cereal systems on productivity and soil fertility was the focus of studies by Carberry et al. (Stylosanthes, Sorghum [46]) and Probert et al. (Chickpea, Wheat [47]). Scenario analysis based

**Figure 4** The modular structure of APSIM that allows modules to be pulled out or plugged in. (Adapted from Ref. 25.)
on historical weather records was also carried out by Keating and Meinke [48], who used APSIM with Wheat and Sorghum and historical weather records to assess exceptional drought in grain-producing areas of northeast Australia.

4 IMPLEMENTATION OF THE HELYAR–PORTER PROTON BUDGET FRAMEWORK

The proton budget of Eq. (1) can in principle be applied to a system at any scale. Implementation of the Helyar–Porter framework in the two agricultural systems models implies a change from the whole profile approach taken by most experimental studies to that of a multilayered soil system. The corresponding changes in system boundaries require modification of the definitions of some of the proton budget terms. These modifications and other aspects, such as the impact of a shift from an annual to a daily time step, are discussed in this section.

4.1 System Boundaries and Implications for Proton Budget Terms

In the “original” application of the Helyar and Porter framework to a whole soil profile, the plants (dead and alive) were included in the system. Effectively, the system was defined by the boundaries of the farm field and the bottom of the root zone. Additions and exports [ad and ex terms in Eq. (1)] occurred at these boundaries (see Fig. 5a). For example, OAex represented the alkalinity in exported products, NO3ex the nitrate leached below the root zone, and NH4ad any ammonium fertilizer added.

This definition of the system allowed certain simplifications to be made. Excretion of protons or bicarbonate ions at the surface of roots due to imbalances in ion uptake (“root excretion” [49]; see also Chapter 3) could be ignored as it was inside the system and because the return of organic anions in residues was not taken into account either. Only the proportion that matched alkalinity in exported products was taken into account (acidifying effect of OAex term). Uptake of nitrate and ammonium was not included in the NO3ex and NH4ex terms, as it too was defined to occur within the system. This exclusion of uptake was possible because the corresponding excretion of protons and bicarbonate ions was not taken into account.

Application of the Helyar and Porter framework to multilayered soil systems does not allow these simplifications, as the amount of proton/bicarbonate excretion varies with depth. In addition, its location is different from that of the alkalinity that is returned in the form of organic anions in residues. The additions and exports now happen at the soil–plant interface and at the boundaries between layers (Fig. 5b). This also means that transport within the profile must be taken into account: exports from one layer are additions to the next layer. Transport of aluminum, which could be ignored in the whole profile treatment, is now an important factor in modeling transport of acidity.
FIGURE 5  System boundaries (thick boxes) and proton budget terms in (a) the “original” application of the Helyar and Porter framework to a whole soil profile and (b) the adapted model implementation for a multilayered soil system. See text for an explanation of abbreviations.
The implementation of the Helyar and Porter framework in multilayered soil systems, therefore, requires the following modifications:

1. additional term for root excretion,
2. inclusion of returned residues in the OAad term,
3. calculation of transport of acidity (including aluminium) between layers.

As a consequence, Eq. (1) has a slightly different form in the implementations in GRAZPLAN and APSIM:

$$\text{Net acid addition} = \frac{\text{nitrogen cycle effects}}{\text{HCO}_3\text{ terms in Eq. (1)}} + \text{net root excretion} + \text{net effect of reactions involving organic anions} + \text{other element cycle effects} - \text{lime dissolution} + \text{net mass flow of acidity}$$

The bicarbonate fluxes in the system [HCO$_3$ terms in Eq. (1)] are included in the net mass flow of acidity. The net effect of reactions involving organic anions refers to the release of alkalinity or acidity from returned plant residues and animal excreta or urine, due to association or dissociation of weak acid groups, the oxidation of organic anions, and the effects of dissociation of weak acid groups following humification of uncharged organic pools. In the “original” Helyar and Porter framework [Eq. (1)] these processes were captured by the OAad and OAac terms. The various processes and their parameters are discussed in more detail in the following.

### 4.2 Proton Production Due to Nitrogen Transformations

The net proton production or consumption due to processes of the nitrogen cycle is calculated in both models according to

$$\text{Nitrogen cycle effects} = \text{net transformation NO}_3 - \text{net transformation NH}_4$$

where net transformation NO$_3$ is the net production of nitrate due to all transformation processes affecting the creation or consumption of nitrate [i.e., reactions (3), (4), and (5) in Fig. 1] and net transformation NH$_4$ is the sum of all transformation processes affecting the creation and consumption of ammonium [i.e., reactions (1), (2), (3), and (6) in Fig. 1]. This definition of the nitrogen cycle contribution differs from that given by Helyar and Porter [4] [Eq. (1)] as the addition and export terms of ammonium and nitrate are not included, whereas those of denitrification and ammonia volatilization are. Plant uptake of nitrate and ammonium [reactions (7) and (8) in Fig. 1] is also not included because the net effects of up-
take of all ions are accounted for in the net root excretion term. Only the protons associated with transformations between the three boxes in Fig. 2 are included, as these are the chemical processes producing or consuming protons (Table 1). This approach of focusing on the actual proton-producing and proton-consuming processes has an advantage over the approach in Eq. (1) because it emphasizes that it is, for instance, not nitrate leaching per se that causes acidification but protons generated during nitrification. Leaching essentially separates nitrate from the protons, ensuring that further transformations will not consume them.

4.3 Net Root Excretion

Root excretion (protons or bicarbonate ions) occurs so that the net charge balance due to uptake of cations (e.g., NH₄, Na, Mg, Ca, and K) and anions (e.g., NO₃, Cl, SO₄, and H₂PO₄) is zero. The effect of absorption of trace elements is usually negligible but may be important in some situations (e.g., for high Mn uptake). The magnitude of acid or alkali excretion from roots is equal to the overall balance of cation to anion uptake. Inside the plant most of the inorganic nitrogen and some of the sulfur is reduced or oxidized into organic compounds. The remaining excess of cations or anions (generally cation excess) is compensated for by organic anions (RCOO⁻).

As decomposition of the plant material causes these organic anions to consume protons, they represent an amount of alkalinity that has been withdrawn from the soil system. Subsequently, this alkalinity may be wholly or partly exported as products and animal excreta or returned as plant residues. The magnitude of the acid excretion from roots due to the uptake of nonmetabolized cations less nonmetabolized anions is equal to the sum of the exported and returned alkalinity. The acid excretion to balance nitrate and ammonium uptake is equal to the difference between these two uptake terms (NH₄ + NO₃). Where the outcome is excretion of bicarbonate ions, the models assume absorption of protons instead, to avoid calculation of the equilibrium between bicarbonate and carbon dioxide in the soil air.

Nitrate and ammonium uptake are simulated dynamically by the two models so that the corresponding absorption or excretion of protons is made to match time and location of uptake. As not all of the other ions are simulated explicitly by the models (GRAZPLAN handles phosphorus and sulfur, APSIM only phosphorus), the proton excretion matching the excess cation uptake needs to be estimated in other ways. The two models handle this slightly differently. It should be noted that both approaches are simplifications of reality because of the limited experimental information on timing and location of ion uptake.

In the GRAZPLAN soil acidity model, the proton excretion due to excess nonmetabolized cation uptake is estimated as the product of the excess cation contents of the shoot and root material and the total net primary productivities of these components. Currently, the values for excess cation content of plant shoots and roots are assumed to be constant characteristics of each plant species. Proton ex-
cretion is distributed between the soil layers in proportion to root mass, but the proportions are weighted according to a decreasing function of layer pH to take account of the concentration gradient against which the root proton pumps must operate [50].

In APSIM, the crops have several aboveground components that have different fates (e.g., harvested products, returned residues) and often different excess cation contents. Dynamic simulation of the corresponding proton excretion during plant development is complicated. For example, in the case of cereals the nutrients that end up in the grain may have been translocated late in crop growth from stem and leaves into grain [51,52]. Hence, the protons that ultimately "match" the alkalinity in the grain may have been excreted before grain development starts. Leaf fall during the season causes similar problems, as it is not reflected in dry matter weights and excess cation contents measured at harvest.

APSIM-SoilpH, therefore, deals with proton excretion due to excess nonmetabolized cation uptake on an event basis. Examples of events are harvest, crop cuts (e.g., lucerne), crop burns (e.g., sugarcane), and leaf fall. Upon occurrence of an event, the excess cation contents of the relevant plant components (e.g., only leaves in case of leaf fall, all aboveground components in case of harvest) are calculated and summed to determine the total proton excretion due to excess nonmetabolized cation uptake since the last event. The disadvantage of this approach is a mismatch in timing—proton excretion due to excess nonmetabolized cation uptake occurs only at predefined events rather than continuously throughout the season. It was deemed, however, that this was necessary to avoid artificial generation of acidity or alkalinity that may occur when calculating daily proton excretion using an "average" excess cation content based on estimated proportions of returned and exported components. Although the APSIM-SoilpH structure includes a component for excess cations in roots, it is not currently considered in the calculations. Root alkalinity or ion concentration data are scarce. This term is, therefore, ignored on the assumption that alkalinity of roots is released in the same layer where protons were excreted.

In calculating the amount of protons excreted in response to excess nonmetabolized cation uptake over nonmetabolized anion uptake (i.e., excluding nitrate and ammonium), APSIM-SoilpH considers the individual ion concentrations rather than the excess cation content. It does so to allow specified profiles for uptake of each ion. Ions are absorbed in proportion to the root length in a layer unless there is reason to believe that the availability of the ion varies significantly between layers. For example, the availability of phosphorus is usually biased heavily to topsoil layers [53,54]. By comparison, the availability of calcium, magnesium, and potassium is often more evenly distributed down the profile [55], so an absorption pattern more closely aligned to root length is appropriate. Where, however, the availability of these cations is known to vary significantly with depth, this can be expressed in the model through the use of ion availability indices.
4.4 Fate of Organic Anions

The fate of organic anions accumulated in the plants varies. Some are returned to the system with plant residues. As discussed previously for crops in APSIM, part of the organic anions may also be exported with products such as cereal grain, sugarcane stem, and pasture hay. In grazed pastures, animals may consume organic anions as part of the feed intake. These organic anions can be returned to the system as feces or urine or be exported via product removal (meat, milk, and wool).

The GRAZPLAN soil acidity model simulates the uptake and excretion by livestock of nutrients and organic anions. Uptake of organic anions follows from the prediction of the intake of energy and protein. The model allows selective grazing and substitution by supplementary feeds and calculates use of the diet for both maintenance and production (e.g., meat, wool, pregnancy, and lactation [28]). An organic anion mass balance is computed for the animals, based on the simulated organic anion contents of their intake and constant organic anion contents for production of wool, fleece-free body weight, and feces [56], with the remaining organic anions excreted in urine. The export of organic anions from the system via product removal (meat, milk, and wool) is estimated by accumulation of the amounts in each day’s animal production.

On a grazed paddock the excretion of feces and urine is not evenly distributed. Sheep camp areas receive large proportions of excreta at the expense of the rest of the paddock [57]. In addition, urine is excreted in patches of locally high nutrient input [58]. In the GRAZPLAN soil acidity model, losses of both nutrients and organic anions due to transfer into camp areas are estimated as a constant proportion of the total excretion. Inorganic nutrient dynamics under urine patches are modeled separately; urine excretion, apart from that in the camps, is assumed to be spread over a small proportion of the field, affecting the rate of uptake by plants and the leaching of urine-derived nitrate.

4.5 Reactions Involving Organic Anions

Oxidation of the organic anions that are returned to the soil consumes protons and hence delivers alkalinity to the system. In addition, association or dissociation of weak acid groups in returned plant residues, animal excreta, and soil organic matter leads to consumption or production of acidity. The effects of these reactions on the proton budget are handled slightly differently by the two models.

In APSIM, return of crop residues is simulated by the crop modules and occurs at events such as harvest and with leaf fall. The organic anion content of the returned material, expressed as (ash) alkalinity, is mixed with that of any residues already on the soil surface. The subsequent fate of the residues is simulated by the residue module. Residues may be burned, incorporated to a certain depth in the soil to become part of the fresh organic matter pool upon tillage, or left to decompose on the surface in response to factors such as moisture, C/N ratio, and temperature.
When surface residues are left to decompose on the surface, the release of alkalinity follows this (slow) decomposition and alkalinity is released upon transfer of carbon and nitrogen from the surface residues to the soil organic (microbial and humus) pools. In the case of residue incorporation, alkalinity is assumed to be released instantaneously. Pot experiments have suggested that, in reality, release of alkalinity due to decomposition from the fresh organic matter pool may take a few days or weeks [59–61], so that there may be a small timing error here.

In APSIM, burning of residues releases alkalinity instantaneously in the surface 5 cm, unless immediately followed by incorporation to a specified depth. In this case, instantaneous release is probably close to reality. Allowance is made for a user-determined loss factor for material blown away in the fire.

APSIM-SoilpH does not keep track of organic anions in the soil. Once surface residues are burned, incorporated, or decomposed into soil organic matter pools, the alkalinity associated with their organic anions is released. Any accumulation or depletion of organic anions in the soil, due to accumulation or depletion of carbon or association/dissociation reactions, is instead estimated from an empirical equation for the organic anion content of soil organic matter and changes in the soil organic matter content. This equation, adopted from Helyar and Porter [4], treats organic anions as Brønsted–Lowry alkalis and takes into account not only their net accumulation but also their change in association/dissociation due to changes in pH. The organic anion content is equated to the cation exchange capacity of the soil organic matter, which is given by

\[ \text{CEC(SOM)} = a(pH - b) \]  

This relationship was derived [4] from measurements of whole soil CEC, clay, and organic matter contents of 60 Wisconsin soils at various pH values [62] and soil humic acid titration curve data presented by Kononova [63]. The parameter \( a \) varies between 0.07 and 0.83 mol kg\(^{-1}\) soil organic matter, depending on the density of pH-dependent groups in the organic matter (usually higher in more decomposed material). The parameter \( b \) represents the pH for zero charge of the organic matter. Helyar and Porter [4] arrived at a value of 1.5 for \( b \), based on the data in Helling et al. [62] and Kononova [63]. For organic-rich soils in New Zealand, De Klein et al. [64] derived a value of about 3. Both \( a \) and \( b \) are user-defined inputs to APSIM-SoilpH, to accommodate the comments by Porter et al. [15] and Poss et al. [17] that the \( a \) and \( b \) values suggested by Helyar and Porter [4] contain some uncertainty due to being quantified for only a narrow range of soils.

To determine the accumulation or depletion of organic anions, the pH-dependent organic anion content needs to be multiplied by the change in organic matter content. This is based on changes in the microbial and humus pools predicted by the soil nitrogen module and a factor between 1.7 and 1.9 (user defined) to convert organic carbon to organic matter [4]. Accumulation of organic anions
is equated to proton production in the proton budget [Eq. (3)], with depletion representing proton consumption.

The preceding approach of APSIM-SoilpH to handling reactions involving organic anions is similar to the original Helyar and Porter framework with its OA$_{ad}$ and OA$_{ac}$ terms. It is a simplification of reality. Due to the daily time step of the model, the approach causes some errors in the timing of alkalinity release, especially with incorporated residues. The errors are only temporary, however, lasting for periods of a couple of weeks to a cropping season at most, and would hence be acceptable for most model applications.

In contrast to APSIM-SoilpH, the GRAZPLAN soil acidity model does keep track of organic anions (or their proton equivalents) in the soil. In this model organic matter is contained in four organic matter pools (labile and resistant fresh organic matter, microbial biomass, and humus). The sizes of these pools are defined in terms of organic carbon (C). The organic anion contents of the pools are expressed as ratios of the proton equivalents to organic carbon (H/C ratios). Decomposition of the organic matter is tracked by the transfers of organic carbon between these pools. Three fates are identified for organic carbon: synthesis into microbial biomass, respiration as CO$_2$, or conversion into humus. Alkalinity associated with synthesized organic carbon is moved to the microbial biomass pool (as organic anions), while that associated with respired carbon is released and taken into account in the proton budget [Eq. (3)]. The conversion to humus takes into account the H/C ratios of the newly formed humus and that of the existing humus pool. The latter is assumed to be dependent on soil pH in a similar way as expressed by Eq. (5). In case of an imbalance between the two ratios, protons are consumed or produced, a process that is reflected in the proton budget [Eq. (3)]. The model uses an $a$ value [Eq. (5)] appropriate for humic acids (0.83 molc kg$^{-1}$) and an OM/C ratio of 1.72 [65].

Upon incorporation of plant residues (physical movement due to mesofauna, trampling, and pugging), only a proportion of their alkalinity is released immediately:

$$\text{Alkalinity released immediately} = \text{total alkalinity} \times \left[ 1 - \frac{\text{soil pH} - 1.5}{\text{plant pH} - 1.5} \right]$$ (6)

where a plant pH of 6.0 is assumed. This equation is based on Eq. (5) and assumes that following equilibration from a plant pH of 6.0 to the soil pH, part of the organic anions $[(\text{soil pH} - 1.5)/(\text{plant pH} - 1.5)]$ remain intact and dissociated. These organic anions are then transferred to the labile and resistant soil fresh organic matter pools, where alkalinity is released upon further decomposition. Organic anions contained in feces are added to the resistant fresh organic matter pool as the feces degrade and enter the soil. Alkalinity associated with organic anion inputs of urine is released immediately and hence contributes, along with alkalinity released from plant residues, directly to the proton budget [Eq. (3)].
4.6 Cycles of Other Elements

A number of other nutrient cycles contribute to the proton budget, for example, redox reactions involving iron and manganese; weathering reactions involving Ca, Mg, K, P, and S; cation exchange; adsorption reactions; and formation of complexes with organic matter. The inorganic soil reactions in response to acid or alkali addition to the soil are not individually accounted for in the Helyar and Porter framework but are instead reflected in the pH buffer capacity used to convert the net proton production into a pH change. The only other cycle currently considered is the sulfur cycle in the GRAZPLAN soil acidity model. It optionally calculates the changes of the proton budget associated with sulfur oxidation/reduction using the same principles as outlined in Helyar and Porter [4]. The oxidation of 1 mole of elemental sulfur or organic sulfur to sulfate generates 2 moles of protons. The same amount of acidity is consumed when sulfate taken up by the plant is being reduced (see Sec. 4.3).

4.7 Lime Dissolution

Addition of lime is currently simulated only by APSIM-SoilpH. Lime dissolution is calculated from the size of the lime pool in a soil layer, the flow of water into the soil layer, and a function describing the solubility of lime as a function of soil pH. This function is a linear interpolation of dissolution data presented by Cregan et al. [66]. A lime dissolution submodel is also planned for the GRAZPLAN soil acidity model.

4.8 Net Mass Flow of Acidity

In both models, transport of acidity and alkalinity in the soil is calculated at each time step as the product of water flow and ion concentration. Ions involved are \( \text{H}^+ \), \( \text{OH}^- \), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), and \( \text{Al}^{3+} \). Activities of the first four ions are calculated using the constants of standard chemical equilibrium reactions [67]:

\[
\begin{align*}
\text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{OH}^- & \log K = -14.00 \\
\text{CO}_2(\text{g}) + \text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{HCO}_3^- & \log K = -7.82 \\
\text{HCO}_3^- & \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} & \log K = -10.33
\end{align*}
\]

(6a)

It is noted that at present the models do not simulate \( \text{CO}_2(\text{g}) \) and, therefore, use a user-specified partial pressure of \( \text{CO}_2(\text{g}) \) in the soil air. As the \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) concentrations are quite sensitive to the partial pressure of \( \text{CO}_2(\text{g}) \) above pH 5.5, the input value for \( \text{CO}_2(\text{g}) \) should take into account the expected level of biological activity in the soil in question.

Transport of aluminum is based on empirical equations. GRAZPLAN uses

\[ p\text{Al}_{tot} = 8.58 \times (p\text{H} - 2.84) / (p\text{H} - 1.35) \]

(7)
where \( p_{\text{Al}_{\text{tot}}} \) is the negative \( \log_{10} \) of the total activity of Al in the soil solution. This equation was fitted to data reported in Helyar et al. [68] and has, in a slightly different form, previously been used in the SPAM model [22,23]. APSIM-SoilpH uses a linear equation with parameters that are user defined and can be adjusted for soil type and difference between topsoil and subsoil

\[
p_{\text{Al}} = a \times \text{pH} + b
\]  

(8)

Depending on the experimental method used to determine \( a \) and \( b \), \( p_{\text{Al}} \) refers to the negative \( \log_{10} \) of the activity of total Al or only \( \text{Al}^{3+} \).

The preceding equations determine the activity of \( \text{H}^+ \), \( \text{OH}^- \), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), and \( \text{Al}^{3+} \). These are converted to concentrations using activity coefficients, which are calculated according to a simplification of the extended Debye–Hückel equation [69]:

\[
\log \gamma_i = -AZ_i^2 \left( \frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3\mu \right)
\]  

(9)

where \( \gamma_i \) is the activity coefficient of ion \( i \), \( Z_i \) is its valency, \( A \) is a constant (0.509), and \( \mu \) is the ionic strength of the soil solution. Currently the ionic strength is a constant, user-defined input. It is important that a value relevant to wet conditions is chosen, as this is when most transport occurs. The “net mass flow of acidity” term in Eq. (3) includes the \( \text{HCO}_3^{\text{ad}} \) and \( \text{HCO}_3^{\text{ex}} \) terms of Eq. (1). The \( \text{HCO}_3^{\text{ac}} \) term of Eq. (1) is assumed negligible. Transport of \( \text{CO}_3^{2-} \) would be a minor component under most soil conditions but was added in APSIM-SoilpH to allow a future chemical description of lime dissolution. Future developments may also consider leaching of soluble organic molecules or organic matter movement between layers by soil fauna.

4.9 Choice of Method for Expressing pH

The definition of pH is the negative \( \log_{10} \) of the activity of protons in solution. The pH of the soil solution is, however, not easy to determine experimentally. In practice most determinations of soil pH are therefore based on a soil extraction procedure. Several different ionic strengths and soil/extractant ratios have been used in the extraction procedures to minimize changes in the distribution of ions between the soil solution and the soil surfaces. The extract pH that best reflects solution pH and the relationships between different pH measurements are dependent on soil type [70–74].

The acidification models can, in principle, operate with pH determined by any method. However, there must be consistency between all parts of the model, including pH buffer capacity calculations. Thus, it is a user decision. In most cases this will be the pH in a 0.01 or 0.002 M CaCl\(_2\) extract. Only when used in chemical equilibrium equations (e.g., for calculation of transport) should the pH really be that of the soil solution. For that purpose, either it needs to be assumed that ex-
tract pH approximates solution pH to an acceptable level or an equation that relates the two pH values needs to be used. As the latter equation would be soil type dependent, care needs to be taken that it forms a consistent set with the initial pH and pH buffer capacity values.

4.10 pH Buffering

The net acid addition [Eq. (3)] can be converted to a pH change using the pH buffer capacity of the soil [Eq. (2)]. The pH buffer capacity lumps together a number of proton-consuming processes such as cation exchange, mineral weathering, and formation of complexes with organic matter. The units of the pH buffer capacity are mol H\(^+\) kg\(^{-1}\) (pH unit)\(^{-1}\) and reflect the slope of a titration curve. As this slope is approximately constant between pH 4.5 and 6.0 [75], a single pH buffer capacity value is often used [4]. This single pH buffer capacity ignores the dissolution reactions of carbonate minerals and aluminum and iron hydrous oxides and hence should not be extrapolated to pH values above approximately 6.5 and below approximately 4.5. As can be expected given the nature of the buffering processes, the pH buffer capacity is soil specific and varies with factors such as cation exchange capacity, soil mineralogy, and clay and organic matter content. Several empirical regression equations have, therefore, been developed to predict the pH buffer capacity from more easily measured parameters, for example, organic matter and clay contents [76], organic carbon and clay contents [77–79], organic carbon, clay, and silt contents [13]. The effect of organic matter is particularly relevant, as organic matter contents can change quite dramatically over the longer time periods that are typically used in model simulations.

The structure of APSIM-SoilpH therefore allows regression equations to be built into the model. The parameters that are simulated by one of APSIM’s modules (e.g., organic carbon content) can then change the pH buffer capacity dynamically as part of the simulation. The rapid increase in buffering at low pH (< 4.0) due to aluminum dissolution is described as a function of exchangeable aluminum. User input of pH buffer capacity is also possible.

In the GRAZPLAN soil acidity model, the soil pH buffer capacity is computed as the sum of three terms. The first term represents the buffering capacity of the soil mineral phase, which remains constant during the simulation. The second term represents the buffering capacity of the soil organic carbon and shifts in response to changes in the organic carbon content of the soil. The third term varies with the concentration of Al\(^{3+}\) in the soil and takes account of the buffering processes due to enhanced dissolution of soil minerals at low pH values. In order to parameterize a simulation, the user needs to specify the initial soil pH buffer capacity and the pH buffer capacity of the organic matter. If there are no measured values available, the software offers the option of estimating values based on empirical equations. The initial soil pH buffer capacity, the initial carbon content, and...
the initial pH are then used to estimate the constant pH buffer capacity term at the start of the simulation.

Time is an important factor in pH buffering processes. For the same total acid production, a high acid production rate will cause a larger pH drop than a slow acid production rate [80]. Although the pH buffer capacity is defined as “the measure of the rate of acid or alkali addition per unit change in soil pH” [4], the word “rate” in this definition does not have a time aspect. Time is a factor only in the experimental determination: the time of equilibration, which may affect the experimental results. Although it has been acknowledged that this is a factor of uncertainty in the application of the Helyar and Porter framework [12–15], little attention has been given to the fact that the pH buffer capacity that is used must be appropriate for the time scale of the period over which the net acid production was determined. For models, such as APSIM-SoilpH and the GRAZPLAN soil acidity model, that generally operate on a daily time step, this issue may be more critical than for the longer term experimental applications of the Helyar and Porter framework. Currently, the models use a daily time step for the calculation of the net acid production and pH change, which is shorter than that of most experimental methods used to determine the pH buffer capacity. The implications that this may have will need to be studied further. It may be necessary to increase the calculation time step, or it may prove more appropriate to distinguish buffer rate and buffer capacity, concepts introduced by Kauppi et al. [81] (RAINS model). They defined the buffer rate as “the maximum potential rate of the reaction between buffering compounds and the hydrogen ions” and the buffer capacity as “the gross potential, the total reservoir of the buffering compounds.” The distinction between the two terms allowed them to capture situations where buffer capacity was high but the buffer rate limited proton consumption.

This discussion highlights the (current) uncertainty in the choice of an appropriate buffer capacity for use in simulations. As pointed out by Ridley et al. [14] and Porter et al. [15], uncertainty in pH buffer capacity may be a reason for the wide variability in acidification rates reported in the literature. The advantage of the models is that the effects of uncertainty in model input can be easily assessed via a sensitivity analysis. Uncertainty bounds can then be specified for model outputs. It is important to remember that there will not necessarily be a linear relationship between uncertainty in the pH buffer capacity and uncertainty in predicted pH change. The model includes various feedbacks (see next section), which will make this a nonlinear function. Uncertainty bounds will strongly depend on the scenario of the simulation (weather, soil type, management).

### 4.11 Feedbacks in the Models

Soil pH affects several processes that are represented in the APSIM and GRAZPLAN models. These include processes described in the acidity models (dynam-
ics involving organic anions, lime dissolution, transport of acidity) but also processes in the soil nitrogen models. For example, urea hydrolysis is influenced by pH, as is nitrification. In the latter case, the pH feedback provides a natural limitation of acidification due to the nitrogen cycle. Nitrification will progressively slow down when the pH drops below pH 6 and is assumed to cease completely at about pH 4.5 (user input in APSIM). Acid production by this key process of the nitrogen cycle will, therefore, stop as well. The rising ammonium concentration may lead to increased ammonium uptake with a corresponding increase in excretion of protons. Compared with the situation of nitrification and nitrate uptake in the same layer, this does not have an effect on the proton budget, but when contrasted with the situation of nitrate leaching out of the layer, there is still a reduction in acid production.

Crop feedback is not yet included in the models, and in instances where “tolerant” plants are being simulated, feedbacks may have little relevance. It is likely to be critical for long-term runs where the soil acidifies strongly or where “sensitive” species are being simulated. It is, however, not a straightforward matter, as there are many ways in which acidification can negatively affect crop growth (H, Al, Mn toxicity; inhibition of Mg, Ca, and K uptake; decrease in P and Mo solubility; inhibition of root growth [82]). The most influential factors are likely to vary from crop to crop, but aluminum toxicity will often be one of them. It appears that aluminum toxicity does most of its damage by impairing root growth and function in a small zone just behind growing root tips. Presumably, there is no simple function that predicts aluminum damage to roots or the influence of tolerance mechanisms.

5 CASE STUDY 1—ACIDIFICATION UNDER WHEAT: SIMULATIONS WITH APSIM-SOILPH

To illustrate the use of APSIM-SoilpH, we present simulations of the wheat experiment reported in Poss et al. [17] and compare model outputs with their assessment of acidification in this system. As the experiment covered only one cropping season, we use the model to extrapolate in time in order to determine how representative the 1993 year was. The model is also used to study the pH profile development over a 12-year period and to determine the effects of fertilizer management.

5.1 Experiment Reported by Poss et al. (1993)

The experiment was conducted at Charles Sturt University (CSU) near Wagga Wagga, New South Wales, Australia. The field was sown to wheat (Triticum aestivum L. cv. Janz) in 1993. Details of the experiment are given by Poss et al. [17], Dunin et al. [83], and Smith et al. [84,85]. Briefly, wheat was sown on June 6,
1993 in two adjacent 5-ha areas identified as the fertilized and unfertilized treatments. Both received diammonium phosphate (DAP, 17 kg N ha\(^{-1}\), 25 kg P ha\(^{-1}\)) drilled with the seed at sowing, but only the fertilized treatment received a top dressing of 140 kg N ha\(^{-1}\) as urea on August 6, 1993. The crop was harvested on December 9, 1993. Prior to sowing, the surface residue of the previous wheat crop was burned (March 31, 1993), the ashes and unburned straw being incorporated (April 15, 1993). Weeds were most likely present during the fallow, but no details on date of appearance or cover were available.

The soil was a red kandosol [86] (previously known as a red earth). Its texture changes from sandy clay loam in the surface (0 to 15 cm) to medium clay in the subsoil. The B horizon has limited structure and a low permeability. The soil is common in the Wagga Wagga district [87]. Soil water and mineral nitrogen contents were measured at regular intervals, as well as crop growth and nitrogen uptake. Both the fertilized and unfertilized treatments contained a weighing lysimeter and were instrumented with ceramic suction cups [88] and time domain reflectometry (TDR). Net mineralization rates of the topsoil (0 to 10 cm) were determined by in situ incubations [85]. Cumulative water flux and nitrate leaching at 25 and 90 cm were calculated from lysimeter and TDR results combined with solution nitrogen contents [17,83,84,88]. To calculate the various proton budget terms [Eq. (1)], measurements were also made of the amount and ash alkalinity of surface residue, crop nutrient concentrations, pH and nitrate concentration of rain, and soil aluminum and manganese concentrations. In addition, the pH buffer capacity was determined [17].

5.2 Parameterization of the Model

For the simulations presented here we used APSIMv1.6 configured with the SoilpH module, the Soilwat2 water balance module, the Nwheat crop module, the SoilN2 soil nitrogen module, and the Residue2 surface residue module. The Manager and Operations modules were used to simulate soil and crop management.

The simulations started on December 15, 1992 after the harvest of the previous wheat crop. Locally measured daily rainfall was available from June 1993. Data from the nearby NSW Agricultural Research station were used prior to that date. Maximum and minimum temperature and radiation data were from the Wagga Wagga Meteorological Office at Forest Hill (located approximately 25 km from the experimental site).

The soil profile (0 to 2 m) was divided into 10 layers, the first of which was 0 to 10 cm. Profiles of the lower limit and drained upper limit for the water balance calculations of the SoilWat2 module were obtained from the driest and wettest profiles observed during the 1993 fallow and cropping season. This resulted in 30.5 mm total plant-available water in the topsoil (0 to 25 cm) and 65.5 mm in the subsoil (25 to 90 cm). Saturation values were obtained from in situ mea-
surements following ponding. The initial water content profile was based on measurements made on March 3, 1993. This assumes no increase in soil water storage from December 15 until March 3. The simulation confirmed that indeed all rainfall during this period was lost through evaporation. A runoff curve number of 75 was chosen on the basis of the sandy clay loam texture of the topsoil. Diffusivity constants (44 and 16) were those appropriate for the clay subsoil. To obtain close agreement with the evaporation data obtained from the lysimeters, it was necessary to use different evaporation parameters (U and cona) for winter (2 and 2) and summer (6 and 3.5) conditions. Others have made similar observations (N.I. Huth and S. Asseng, personal communication, 2000), notably that the rate of second-stage evaporation is not independent of evaporative demand.

Profiles of bulk density, initial organic carbon, and pH were as measured at the site in 1993. Low initial mineral nitrogen content was assumed, on the basis that most nitrogen would have been taken up by the 1992 crop. The CO₂ partial pressure in the soil was assumed to be 0.3 kPa [67]. Parameters of the pAl-pH relationship [Eq. (8)] were based on data from a field experiment near Wagga Wagga (K. R. Helyar et al., unpublished). The initial weight of surface residues (11 t ha⁻¹) was an estimate based on the size of the previous crop. It was slightly higher than the 9.7 t ha⁻¹ reported by Poss et al. [17] as this measurement was made in March, 3 months into the fallow. Ash alkalinity of surface residues, pH buffer capacity, and pH of rainfall were taken from Poss et al. [17]. Nutrient concentrations in the crop were those measured at harvest. The initial root residues and their C/N ratio were estimated on the basis of the size of the crop in 1992 and typical values obtained in a 12-year continuous wheat simulation (see later). The last two parameter values are a source of uncertainty in this simulation. The urea application in the fertilized treatment was reduced to 120 kg N ha⁻¹ to allow for volatilization losses that were not accounted for by the model (estimated to be 10 to 25 kg N ha⁻¹ [85]).

Standard values were chosen for the model constants in Soilwat2, SoilN2, and Residue2 [26], with the following exceptions. Like Asseng et al. [43] and Snow et al. [89], we found it necessary to increase the magnitude of parameters controlling potential mineralization. We chose to use the value of 0.00025 day⁻¹ of Snow et al. [89] for the potential decomposition rate for the humus pool (rhum) and increase the daily potential decomposition rate for the soil biomass pool (rdbiom) in proportion to 0.0135 day⁻¹. The potential decomposition rate of residue was lowered to 0.02 day⁻¹, down from the 0.1 day⁻¹ proposed by Probert et al. [26] based on a study at Warra, Queensland. The higher value required in Queensland seems to be associated with the relatively few days that are predicted to have adequate moisture for decomposition to proceed. In addition, the efficiency of carbon retention upon decomposition of organic matter or residues was reduced from 40 to 30%, which effectively reduces the immobilization demand when cereal residues decompose. This was based on experiences at other locations.
where a tendency has been found for the model to underpredict mineralization and crop uptake of nitrogen if large amounts of cereal residues are present.

APSIMv1.6 does not have a standard module for weeds. We, therefore, re-configured the Nwheat module to represent a grassy weed species. This was achieved by eliminating carbon allocation to grain, selecting an extended time to flowering, and limiting rooting depth to 50 cm. A similar approach to simulating the effects of weed competition in a maize rotation has been reported by Keating et al. [90]. Fischer et al. [91] also used a modified wheat model (WEEDGRO) to simulate weed growth during fallow periods in wheat systems in southern New South Wales. The weed germination scheme was adopted from Fischer et al. [91], with weeds germinating on the first rain event after December 1 that exceeded 25 mm (December to February) or 20 mm (March to April 10) over two consecutive days. Weeds were killed and incorporated at the tillage event on April 15. Fischer et al. [91] allowed weed growth in May as well. They found that their scheme correctly predicted 14 out of 18 experimentally observed waves of weed emergence.

As no experimental details on weed growth were available and parameterization of the model was not fully independent of the data used to evaluate the performance of the model, the simulations are not a validation of the model. The simulations are, however, still suitable for testing confidence in the model’s description of water and nitrogen cycling due to the extensive and detailed nature of the experimental data set, which includes information on distributions of water and nitrogen in the soil profile as well as fluxes such as evapotranspiration, nitrate leaching, mineralization, and uptake of nitrogen. Thus, there are adequate data to ascertain that the model is simulating the important processes involved in the dynamics of soil water and nitrogen with an acceptable degree of accuracy.

5.3 Simulation of Experimental Data and Comparison with Observations

The simulation results for the unfertilized and fertilized treatments were compared with the measured profiles of water content and mineral nitrogen during 1993. Changes in water and nitrogen contents and the movement of nitrate within the profile were simulated satisfactorily (data not shown). Agreement with measured evapotranspiration was also reasonably good, except for a small underprediction at the end of the season in the unfertilized treatment. Patterns of cumulative water flux and nitrate leaching, therefore, compared well with the data presented by Poss et al. [17] and Smith et al. [84] (Fig. 6).

The effect of weeds during the preseason fallow in 1993 was small. The largest effect was on nitrate leaching past 25 cm, which was predicted to accumulate to 40 kg N ha\(^{-1}\) in the absence of weeds, still within the maximum observed range (not shown). The weeds germinated on December 27, 1992, emerged 4 days
later, and reached a maximum leaf area index (LAI) of 0.037 and a maximum aboveground biomass of 230 kg ha\(^{-1}\).

The patterns of crop growth [85] were simulated satisfactorily. Predicted dry matter biomass (8.6 t ha\(^{-1}\)) and grain yield (3.3 t ha\(^{-1}\)) of the unfertilized treatment were slightly below the measured values (10.9±1.7 and 3.8±0.7 t ha\(^{-1}\), respectively; mean ± SD). The values of the fertilized treatment (biomass of 17.4 t ha\(^{-1}\) and grain yield of 6.2 t ha\(^{-1}\)) compared well with those measured (16.1±1.0 and 6.8±0.9 t ha\(^{-1}\), respectively). Nitrogen uptake by aboveground biomass was comparable in the unfertilized treatment (70 predicted vs. 72±18 kg N ha\(^{-1}\) measured) and slightly high in the fertilized treatment (176 vs. 165±16 kg N ha\(^{-1}\)). Total mineralization for the fallow and cropping season was 150 kg N.
Mineralization during the cropping season was predicted to be 52 kg N ha\(^{-1}\) in the surface 10 cm.

The proton budget predicted by the model highlights the different rates of acidification of the topsoil and subsoil (Table 2). In both the fertilized and unfertilized treatments, the topsoil (0 to 25 cm) acidifies and the subsoil undergoes a net alkalinization. The nitrogen cycle is the main cause of acidification in the topsoil.

Net proton excretion by roots is important as well, largely due to the prediction of significant uptake of ammonium. Poss et al. [17] estimated a much smaller contribution of ammonium uptake, which was limited to the subsoil (Table 2). Experimental data on the form of nitrogen uptake were not available. The Nwheat module uses an uptake routine similar to that of CERES-Wheat [92], in which soil supply of nitrate and ammonium is a function of their concentrations in the soil. With most mineralization occurring in the topsoil, this is where the model predicts most ammonium uptake. However, because the source of the nitrogen was largely organic nitrogen and urea (reference forms in the Helyar and Porter framework, Fig. 2), the form in which nitrogen is taken up has no effect on the proton balance when uptake occurs in the same layer as nitrification. It affects only the relative magnitudes of the nitrogen cycle and root excretion terms. In the case of the fertilized treatment, a dry spell shortly after the urea application and rapid uptake by the crop minimized nitrate leaching, so that the effect on the proton balance would be minor.

Total nitrogen uptake was higher than presented in the proton budget of Poss et al. [17] (Table 2) because they considered only uptake by aboveground biomass, whereas the model predictions included nitrogen uptake by roots. This also accounts for the enhanced alkalinization of the subsoil. The main source of alkalinity in the topsoil is returned residues. The model predicts a small role for the depletion of organic anions. This may be explained by the fact that the proton budget presented here included the return of root residues, which limited the decline in soil carbon.

Similar to the findings of Poss et al. [17], the contribution of mass flow was small. This term would, however, become more important if the topsoil acidified further. Despite small differences in the proton budget terms, in general the simulations are consistent with the assessment of Poss et al. [17] that whereas overall profile acidification was small, acidification occurred in the topsoil.

### 5.4 How Representative was 1993?

Detailed experiments such as the one presented by Poss et al. [17] can be carried out for only a limited period and hence will sample only a small fraction of the weather patterns. To check how representative the experimental year 1993 was, we ran a long-term simulation scenario based on historical weather data (SILO...
<table>
<thead>
<tr>
<th>Budget term</th>
<th>APSIM-SoilpH simulation</th>
<th>Poss et al. [17] analysis: selected terms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unfertilized</td>
<td>Fertilized</td>
</tr>
<tr>
<td></td>
<td>0 to 25 cm 25 cm</td>
<td>0 to 25 cm 25 cm</td>
</tr>
<tr>
<td>Nitrogen cycle effects</td>
<td>4.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Root excretion</td>
<td>0.1</td>
<td>−2.9</td>
</tr>
<tr>
<td>NO₃ uptake</td>
<td>−3.8</td>
<td>−3.3</td>
</tr>
<tr>
<td>NH₄⁺ uptake</td>
<td>2.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Cation excess</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Returned organic anions</td>
<td>−2.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Depletion of organic anions</td>
<td>−0.7</td>
<td>−0.1</td>
</tr>
<tr>
<td>Net mass flow of acidity</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td>1.5</td>
<td>−2.0</td>
</tr>
</tbody>
</table>

ᵃValues for depletion of organic anions and for Total of Poss et al. analysis are based on a 2% per year mineralization rate of organic matter, as the experimental rate of mineralization (3.5% per year) was probably an overestimate [17,85].
Patched Point Dataset*) from the Meteorological Office at Forest Hill close to the experimental site. The simulation consisted of repeating the preceding scenario of a wheat crop following a summer fallow each year from 1958 to 1997. In the simulations, wheat was sown within a window from May 1 until June 15. The conditions for sowing included 30 mm rain in the last 10 days, less than 1 mm rain the previous day, no rain on the day, and soil water in the 10- to 15-cm layer exceeding 50% of plant-available soil water storage. If no sowing opportunity arose before June 15, the crop was sown “dry” on that day. Fertilizer management reflected the 1993 experiment with 17 kg N ha\(^{-1}\) ammonium applied at sowing as DAP and 120 kg N ha\(^{-1}\) as urea 62 days later (fertilized scenario only). The crop was harvested 12 days after maturity (as in the 1993 experiment), after which crop residues were left on the surface. These were 95% burned on March 31 and the remainder incorporated on April 15. Weeds were allowed to germinate following the scheme of Fischer et al. [91] (see earlier). Soil and crop parameterizations were identical to those of the 1993 simulations. Soil water, soil nitrogen, surface residue, and soil pH parameters were reset after every harvest to the conditions that existed after the harvest in 1992 so as to focus on the effects of weather patterns during the fallow and crop on proton-producing and proton-consuming processes without the confounding effects of carryovers from the previous season.

Rainfall in 1993 at the experimental site was significantly lower than that at Forest Hill, which is approximately 25 km away (592 mm vs. 733 mm). As shown in Table 3, the higher rainfall particularly affected the cumulative water flux and nitrate leaching below the root zone (≥ 70% increase). Nitrate leaching at 25 cm was affected less. Acidification of the topsoil was, therefore, only slightly higher (≤ 20% increase).

The year 1993 was a very wet year within the 1958 to 1997 rainfall record of Forest Hill. Annual rainfall exceeded the 85th percentile, and monthly rainfall during July (130 mm), September (121 mm), and November (97 mm) exceeded the 90th percentiles for these months. Cumulative water flux at both 25 and 90 cm was, therefore, above average (both 76th percentile). Despite the relatively dry weather in August (27 mm, 17th percentile) and the rapid nitrogen uptake by the crop following the urea application, the amount of nitrate that leached past 25 cm still ranked at the 79th percentile (Fig. 7). Timing of fertilizer application in relation to crop nitrogen demand is, however, a critical factor in determining nitrate leaching. The large amount of nitrate leached in 1976 illustrates this. Rainfall during 1976 was below average, with very little rain from March until August (66

---

*) SILO is a meteorological information service for rural industries (www.bom.gov.au/silo/). As part of this service, the Patched Point Dataset was developed by the Queensland Department of Natural Resources. It combines original Bureau of Meteorology measurements for a particular station with interpolated data to provide a continuous meteorological data set. For more information, see http://www.dnr.qld.gov.au/silo/
TABLE 3  Selected Model Outputs for the Period December 15, 1992 to December 15, 1993 Using Two Different Rainfall Records (Distance Approximately 25 km)

<table>
<thead>
<tr>
<th>Model output</th>
<th>Local rainfall</th>
<th>Forest Hill Met station</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unfertilized</td>
<td>Fertilized</td>
</tr>
<tr>
<td>Rain (mm)</td>
<td>592</td>
<td>592</td>
</tr>
<tr>
<td>Evaporation (mm)</td>
<td>309</td>
<td>278</td>
</tr>
<tr>
<td>Transpiration (mm)</td>
<td>158</td>
<td>279</td>
</tr>
<tr>
<td>Cumulative water flux at 25 cm (mm)</td>
<td>174</td>
<td>151</td>
</tr>
<tr>
<td>Cumulative water flux at 90 cm (mm)</td>
<td>104</td>
<td>63</td>
</tr>
<tr>
<td>Nitrate leaching at 25 cm (kg N ha⁻¹)</td>
<td>34</td>
<td>36</td>
</tr>
<tr>
<td>Nitrate leaching at 90 cm (kg N ha⁻¹)</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Net acidification in the 0 to 25 cm layer (kmol H⁺ ha⁻¹)</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Net acidification in the 25 to 90 cm layer (kmol H⁺ ha⁻¹)</td>
<td>−2.0</td>
<td>−1.8</td>
</tr>
</tbody>
</table>

FIGURE 7  Variation in simulated annual nitrate leaching at 25 and 90 cm for the fertilized scenario based on the Forest Hill meteorological record. Note that every year conditions were reset to those measured after the 1992 crop.
mm). In the simulation scenario this led to late sowing and poor crop establishment. Because urea application was fixed at 62 days after sowing, this occurred not long before the above-average September rainfall and led to significant leaching from the topsoil.

In the fertilized treatment, acidification of the topsoil is highly correlated with nitrate leaching past 25 cm (0.86 correlation coefficient), causing the acidification rate of the topsoil in 1993 to be above the average, although not as high as in, for example, 1976, despite the much higher rainfall. Compared with the average rates of 1.0 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\) for the unfertilized scenario and 2.5 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\) for the fertilized scenario, acidification in the 0 to 25-cm layer in 1993 was ranked at the 79th and 84th percentiles.

The ranking of 1993 is sensitive to the assumptions made about weed growth in the simulations. When weed-free fallows were assumed (data not shown), the simulations ranked the year 1993 at the 66th and 71th percentiles for topsoil acidification in the unfertilized and fertilized treatments, respectively. The presence of weeds during the fallow keeps the soil drier and hence influences acidification through reduced drainage and nitrate leaching at the break of season. It may also affect preseason mineralization. As the period January to April was relatively dry in 1993, growth of weeds was predicted to be limited (maximum LAI of 0.053 and aboveground biomass of 314 kg ha\(^{-1}\)), compared with the long-term average and maximum values for LAI (0.21 and 0.81) and aboveground biomass (587 and 2619 kg ha\(^{-1}\)). A greater impact of weeds is expected in years with relatively wet fallow periods, so that topsoil acidification in these years is reduced most.

Although the weed growth simulations have been only indirectly tested against evapotranspiration data of the Poss et al. 1993 experiment [17], we nevertheless expect that the simulated level of weed activity is not unrepresentative for cereal systems with similar fallow management. In reality, weed growth, of course, remains highly site specific due to its dependence on fallow management. The preceding analysis should therefore be viewed in the specific context of the chosen scenario. In addition to the uncertainty introduced by weeds, carryover effects, which were excluded from these simulations, may affect carbon and nitrogen dynamics and hence soil acidification.

### 5.5 Topsoil pH Decline and pH Profile Development under Continuous Wheat

The net proton production or consumption in each layer (kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\)) is converted by the model into a pH change using the pH buffer capacity [Eq. (2)]. Continuous simulation scenarios (without resetting) were, therefore, carried out to study the pH profile development under wheat. These scenarios mimicked the conditions of the Poss et al. experiment [17], with an unfertilized (only DAP at sowing, 17 kg N ha\(^{-1}\)) and a fertilized treatment (DAP, 17 kg N ha\(^{-1}\), and top
dressing of urea). A third scenario was included in which no fertilizer was added (N0 treatment).

The pH profile measured in 1993 [17] followed 9 years of cropping and one liming event (1991). It had an acid layer between 10 and 15 cm with a pH (CaCl₂) of 4.5. The pH values of topsoil (0 to 5 cm) and subsoil (70 to 90 cm) were both 5.8. To study how such a pH profile might develop, the initial pH profile for the continuous run was modified to start at 4.9 in topsoil (0 to 10 cm), gradually increasing to 5.1 at 15 to 25 cm and to 5.8 at 50 cm and below. The topsoil pH values match those reported by Heenan and Taylor [93] and Conyers et al. [94] for the start of a cropping rotation trial. Model initialization, crop, soil, and fallow management were otherwise the same as for the scenarios already discussed. To allow the pH buffer capacity to change over time, the model calculated the pH buffer capacity as a function of pH, exchangeable aluminum, effective cation exchange capacity, and the organic carbon fraction [95–97].

The period 1979 until 1991 was chosen to allow a qualitative comparison with data from a 12-year field trial of the effect of management practices on soil pH decline carried out on a similar soil near Wagga Wagga [93,94]. Two of their treatments were continuous wheat with (WW + N) or without (WW − N) fertilizer (100 kg N ha⁻¹ year⁻¹).

In both the unfertilized (DAP) and fertilized (DAP + urea) scenarios, the pH of the topsoil (0 to 10 cm) was predicted to decline steadily (Fig. 8). In the unfertilized treatment, the rate of decline was smaller than in the fertilized treatment. The pH decline of the fertilized scenario compared well with the data presented by Heenan and Taylor [93] for their fertilized treatment (WW + N). Without any fertilizer (N0), the pH of the topsoil did not decline in the simulations. This behavior differed from that of the unfertilized treatment (WW − N) of Heenan and Taylor [93], which was more similar to the DAP treatment, especially in the first 6 years. This is most likely due to differences in initial soil fertility. The experiment of Heenan and Taylor [93] was preceded by 19 years of mostly subterranean clover–based pasture, which would have increased the more labile components of organic matter significantly. Indeed, parallel measurements of soil organic carbon and nitrogen in the unfertilized (WW − N) treatment showed a marked decline in both carbon (6 t ha⁻¹ over 14 years) and nitrogen (0.7 t ha⁻¹ over first 12 years) [98]. These levels of mineralization could not be simulated by the model, which was initialized based on conditions that existed after the harvest in 1992. Reparameterization of the model was considered beyond the scope of this case study. It is interesting to note, however, that the leveling out of pH decline in the later years of the experimental WW−N treatment, when fertility had run down, was similar to the simulated N0 treatment.

Simulation of pH profiles requires specification of very thin layers near the surface due to the rapid changes in pH over the first 15 to 20 cm (e.g., see data from Conyers et al. [94] in Fig. 9). This presented a slight problem for the APSIM con-
The Soilwat2 water balance module, evaporation currently occurs only out of the first layer. Although the drying front can extend beyond this depth due to upward water flow, in some soils this can present problems when layers as thin as 5 cm are chosen. This proved to be the case for the soil from the experiment considered here with its texture contrast between topsoil and subsoil. During the simulation of the summer fallows, the drying front did not extend deep enough, keeping in particular the second and third layers too wet. As a consequence, the mineralization in these layers was predicted to occur earlier than happened in reality, leading to overpredictions of nitrate leaching past 25 cm. The predicted pH profiles presented in Fig. 9 were, nevertheless, obtained using thin 5-cm topsoil layers (0 to 5, 5 to 10, 10 to 15). Due to the overprediction of nitrate leaching, the pH drop in the surface layers is slightly overpredicted, but otherwise the results are consistent with the experimental data presented by Conyers et al. [94].

The problem with thin surface layers may not manifest itself with all soils. Asseng et al. [43] have presented successful simulations of nitrate leaching in a deep sand using the same 5-cm surface layers. The problem could be overcome by
configuring APSIM with the SWIM water balance module, which is based on a numerical solution that would actually improve with thinner layers [27].

### 5.6 Further Comments

Poss et al. [17] suggested that wheat cropping may have contributed little to the observed acidification in the Wagga Wagga region and instead implicated the ley phase in combination with fallow breaks. They arrived at this conclusion by generalizing their findings for 1993, when they observed limited nitrate leaching below the root zone and little overall acidification of the profile despite high rainfall and high drainage. However, whereas the acidification under cropping may be small on a whole profile basis, the proton budget (Table 2) and the data of Heenan et al. [93,94] (Figs. 8 and 9) show that in the zone that matters for crop establishment and early growth (surface 0 to 25 cm) acidification can be significant, especially under fertilized conditions.

The simulations describe the pH profile development under wheat reasonably well, despite the fact that they have not been parameterized specifically for the Heenan et al. cropping trial [93,94]. Although preliminary, the results show that, following additional testing, the model could be a useful tool to explore the

---

**FIGURE 9** The effect of fertilizer application on the predicted pH profiles after 12 years of continuous wheat (lines) and a qualitative comparison with data from similar treatments presented by Conyers et al. [94] (symbols). Treatments as in Fig. 8.
relative contributions to soil acidification of crop and ley phases and the importance of any carryover effects. Testing should focus on the current uncertainties in model parameterization and on the transition from ley to cropping phase. It should consider processes in the subsoil, as the ley phase could be important for deeper acidification, as shown in the next case study (Sec. 6). Such analyses of crop and ley phases would be particularly relevant given the push in recent years to introduce lucerne in cropping rotations to reduce deep drainage. It is important that this introduction is accompanied by management practices that will minimize the effects on soil acidification. Simulation modeling may assist in exploring management options and designing a sustainable rotation.

6 CASE STUDY 2—ACIDIFICATION UNDER PASTURE: SIMULATIONS WITH THE GRAZPLAN SOIL ACIDITY MODEL

This study illustrates the application of the GRAZPLAN soil acidity model to data from the landmark research of Bromfield et al. [21] on soil acidification under subterranean clover–based pastures in the catchment of the Pejar dam, near Crookwell, New South Wales, Australia. They reported that substantial acidification had occurred in a number of soils under long-established pastures. The extent of the decline in soil pH was associated with the length of time since the pastures were established; the largest decline was seen in yellow podzolic soils derived from granite. The case study also demonstrates that the GRAZPLAN soil acidity model can be applied to understanding the relative importance of the processes contributing to soil acidification. It illustrates some of the issues yet to be resolved in modeling these processes and indicates where further research is required.

6.1 Data Inputs for the Simulation

Bromfield et al. [21] measured soil pH in 1980 in pastures established between 26 and 55 years previously and compared the values with those for sites under unimproved native vegetation. When estimating the changes in soil properties with time under pasture, they assumed that the values at the unimproved sites represented the situation 55 years previously. The same assumption was made in the simulation study. Simulations of pasture production on the yellow duplex soil derived from granite, described by Bromfield et al. [21], were made for the period from 1925 to 1980 to mimic the development of soil pH profiles beneath 55-year-old subterranean clover pastures. A wool-growing enterprise was assumed, stocked continuously at nine Merino wethers per hectare with a 20% replacement policy. A minimal feed supplementation policy was selected with wheat fed to the sheep if their condition score fell below 1.0. The pastures in the study area would have comprised mainly annual grasses and subterranean clover, and this was the species composi-
tion assumed in the simulation with the parameter set for the clover cultivar Mt. Barker used. The assumed rate of superphosphate application was 125 kg ha\(^{-1}\) year\(^{-1}\) (9% P content). This was calculated from the rate of increase of total phosphorus in the soil [99] and assuming that 50% of applied phosphorus remained unused in the soil profile. The weather file used to run the simulation was based on Bureau of Meteorology data for Crookwell and nearby localities. For the period from 1957 to 1980 weather data were constructed using the Queensland Department of Natural Resources Data Drill* facility. For the period prior to 1957, radiation and temperature data were generated using Richardson’s [100] generator.

Soil horizon depths, pH buffer capacity, and clay contents were those for soil profile “H” described by Bromfield et al. [21]. The A horizon boundary was set at 40-cm depth on the basis of the change in the clay content. Hydraulic properties were not recorded in the original study and were assumed to be similar to properties measured for a granite-derived, yellow podzolic soil at the Ginninderra Experiment Station, near Hall, Australian Capital Territory, Australia. Phosphorus sorption characteristics of this topsoil were also used in the simulation. Soil bulk densities used in the simulation were the same as in Helyar and Porter [4]. Soil organic carbon, nitrogen, and phosphorus contents were estimated using the equations relating time under pasture to soil nitrogen and phosphorus contents from a study on a similar soil nearby at Binda, New South Wales, Australia [99]. The C/N ratio of soil organic matter was assumed to be 10:1. The initial values for soil pH buffer capacity were deduced using the initial calculated carbon values and a soil organic carbon buffer capacity of 1.44 mol H\(^+\) kg\(^{-1}\) C.

The pH and pH buffer capacity (pHBC) values for soil profile H reported by Bromfield et al. [21] were measured in 1:5 soil/water suspensions. These were converted to pH(CaCl\(_2\)) and pHBC(CaCl\(_2\)) values because the calculations in the GRAZPLAN soil acidity model are based on values measured in 0.01 M CaCl\(_2\). This was based on equations shown in Bromfield et al. [21].

### 6.2 Production Summary

Average pasture production was predicted to be 7.2 t DM ha\(^{-1}\) year\(^{-1}\) (range 2.4 to 19 t ha\(^{-1}\) year\(^{-1}\)). Owing to the effect of phosphorus fertilizer inputs, productivity trended upward from 4.8 to 10 t ha\(^{-1}\) year\(^{-1}\) over the 55 years of the simulation. The average species composition was 36% clover and 64% annual grasses. The average wool clip was 42.1 kg greasy ha\(^{-1}\) year\(^{-1}\) and average net export of sheep live weight was 65.7 kg ha\(^{-1}\) year\(^{-1}\). These are considered to be reasonable figures for production in that district.

* The SILO Data Drill was developed by the Queensland Department of Natural Resources and provides interpolated data for any location in Australia. For more information, see http://www.dnr.qld.gov.au/silo/
6.3 Accumulation of Carbon and Nutrients

Figure 10 shows simulated and measured values of the total nitrogen, organic phosphorus, and total phosphorus content of the soil. The simulated rates of increase in the three nutrient pools were in reasonable agreement with the changes reported by Williams [99].

The slower increase in total nitrogen simulated in the first 25 years and the accelerated increase thereafter were associated with lower and higher pasture yields in these periods, respectively. The higher yields in later years were due to several factors, including improved availability of phosphate as a result of regular fertilizer inputs, increases in soil nitrogen input from the clover with time, and some favorable rainfall seasons (data not shown). Soil organic matter increased as pasture productivity improved, and this, in turn, increased nutrient cycling and hence nutrient availability in the model. Phosphate availability was the key factor governing the productivity of the whole grazing system because phosphorus limitations to subterranean clover growth also limited the acquisition of nitrogen via nitrogen fixation.

![Figure 10](image-url)

**Figure 10** Total nitrogen, total phosphorus, and organic phosphorus contents in the 0 to 10 cm layer of the soil. Broken lines represent regressions fitted to measured data published by Williams [99]. Solid lines represent simulation results.
6.4 Relative Contribution of Different Processes to the Acid Budget

Knowledge of the sources of acid generation and the flow of protons within the system is important for understanding the underlying mechanisms. The contributions of the different carbon cycle and nitrogen cycle terms in the simulation are listed in Table 4 alongside previous estimates by Helyar and Porter [4] for the same site.

The GRAZPLAN soil acidity model calculated a total acidification rate of 3.38 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\) in this simulation. Helyar and Porter [4] estimated the acidification rate to be 3.46 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\) using the pH change between 1925 and 1980 and the pH buffer capacity in 1980 given in Bromfield et al. [21]. However, both values might underestimate the acidification rates. In the simulation, the decrease of the topsoil pH was not as great as the measured pH change (Fig. 11). Bromfield et al. [21] sampled to only 60 cm, and the estimate by Helyar and Porter [4] was based on that soil depth, but an examination of the soil pH pro-

---

**Table 4** Total Soil Acidification and Sources of Acid or Alkali for a Grazed Pasture System on a Yellow Duplex Soil Developed from Granite (Units kmol H\(^+\) ha\(^{-1}\))

<table>
<thead>
<tr>
<th>Acidification component(^a)</th>
<th>Estimates by Helyar and Porter [4]</th>
<th>GRAZPLAN simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55 years Annual % of total</td>
<td>55 years Annual % of total</td>
</tr>
<tr>
<td>Nitrogen cycle terms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{NH}_3\text{H})</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>(\text{NO}_3\text{H})</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>(\text{NH}_4\text{C})</td>
<td>-1.26 -0.02 -0.6</td>
<td>-5.09 -0.09 -2.7</td>
</tr>
<tr>
<td>(\text{NO}_3\text{C})</td>
<td>3.24 0.06 1.7</td>
<td>0.39 0.01 0.2</td>
</tr>
<tr>
<td>(\text{NH}_3\text{E})</td>
<td>0 0 0</td>
<td>0 0 0</td>
</tr>
<tr>
<td>(\text{NO}_3\text{E})</td>
<td>76.9 1.4 40</td>
<td>40.6 0.74 21.8</td>
</tr>
<tr>
<td>Carbon cycle terms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{OA}_{3x})</td>
<td>81.8 1.49 43</td>
<td>118.58 2.16 63.8</td>
</tr>
<tr>
<td>(\text{OA}_{3x})</td>
<td>28.3 0.52 15</td>
<td>33.82 0.61 18.2</td>
</tr>
<tr>
<td>(\text{OA}_{3d})</td>
<td>0 0 0</td>
<td>-1.47 -0.03 -0.8</td>
</tr>
<tr>
<td>Mass flow (H(^+), OH(^-), HCO(_3))</td>
<td>2.0 0.036 1</td>
<td>-0.85 0.016 -0.5</td>
</tr>
<tr>
<td>Total acidification</td>
<td>191 3.46(^b) 100</td>
<td>186.00 3.38(^c) 100</td>
</tr>
</tbody>
</table>

\(^a\) For explanations of the individual acidification components see Eq. (1).
\(^b\) Based on measurements of Bromfield et al. [21].
\(^c\) Based on a dynamic simulation of the production system using daily time steps over 55 years.
files indicated that the soil had acidified below that sampling depth. This implied that the acidification rate was probably higher than the values given in Table 4. Although the estimates of total acidification produced by the simulation were consistent with the calculations of Helyar and Porter [4], the proportionate effects of carbon cycle and nitrogen cycle terms were different. Helyar and Porter [4] attributed 59% of the total acidification to the carbon cycle and 41% to the nitrogen cycle, whereas in the simulation reported here the relative contributions were 81% and 19% respectively. Without measured data for soil carbon or nitrate leaching at this site, the relative proportion of the carbon and nitrogen cycles to acidification there remains uncertain, as discussed in the following.

In the simulation reported here, the carbon cycle was the most important contributor to the acidification rate. The organic anion accumulation, the major carbon cycle term, accounted for 2.16 kmol H⁺ ha⁻¹ year⁻¹ or 64% of the total acidification. In contrast, Helyar and Porter [4] estimated the organic anion accumulation to be 1.49 kmol H⁺ ha⁻¹ year⁻¹, which was equal to 43% of the total acidification. However, this remains an area of uncertainty because the original
values for the soil organic carbon contents of this particular site were unknown and were estimated independently in the two studies using different procedures.

The organic anion export, which comprises organic anions removed in animal products, transported to sheep campsites, and deposited there in dung and urine, was predicted to result in 0.61 kmol H⁺ ha⁻¹ year⁻¹ in the simulation. This explained 18.2% of the total acid budget. In comparison, Helyar and Porter [4] assumed a lower stocking rate in their study and consequently the corresponding estimates were smaller: 0.52 kmol H⁺ ha⁻¹ year⁻¹ and 15% of the total acid budget. In the simulation here, it was assumed that the animals obtained extra supplementary feeding when necessary. The resulting organic anions added would have consumed 0.03 kmol H⁺ ha⁻¹ year⁻¹. Helyar and Porter [4] estimated the net changes due to mass flow of H⁺, OH⁻, and HCO₃⁻ to be acidifying, adding 0.036 kmol H⁺ ha⁻¹ year⁻¹ to the acid budget. In contrast, the simulation resulted in a small negative net mass flow (H⁺, OH⁻, and HCO₃⁻) term of −0.016 kmol H⁺ ha⁻¹ year⁻¹. This can be explained by leaching of hydrogen ions out of the system. In the model, hydrogen ions can move considerable distances downward in short periods of time in major leaching events. It appears that this accounts for the small differences in the mass flow term.

The effects of nitrate and ammonium accumulation in the soil profiles on the acidification rate were small. However, the contribution of the nitrate leaching term (NO₃ex) to the acidification process was very important. In the simulation, 10.3 kg NO₃⁻N ha⁻¹ year⁻¹ was leached beyond the root zone, which equals an acid addition of 0.74 kmol H⁺ ha⁻¹ year⁻¹. Nitrate leaching was calculated from the simulated nitrate concentration and amount of drainage and was favored in years when the clover content of the pasture was high. Nitrate leaching in the simulation was episodic, occurring when the soil profile was saturated and rainfall high. Deposition of high concentrations of urea in urine patches was the key process contributing to nitrate leaching. When the simulation was run without urine patches (i.e., urine was distributed evenly over the whole paddock), very little nitrate was leached below the root zone. In the urine patches, nitrogen inputs exceeded nitrogen uptake by plants and opportunities for nitrate leaching occurred. This is consistent with the report by Ridley et al. [16], where fertilizer nitrogen was applied at rates that are likely to be deposited in urine patches, and nitrate leaching under annual ryegrass pasture was 11, 314, and 32 kg N ha⁻¹ in three consecutive seasons in the nitrogen-fertilized plots compared with 7, 19, and 21 kg N ha⁻¹ in the control plots. At the moment, our modeling of urine patches is rudimentary. We need to know more about the seasonal livestock water balance and the consequences for patch size, the areas in paddocks that are affected by urine, the duration of patch nitrogen influences, leaching of urea within patches, and the transient soil pH changes that occur [101]. These factors influence the nitrogen concentration of the affected soil, the rate at which nitrification proceeds, and, ultimately, the likelihood that nitrate will be leached.
At this stage of its development, the model does not simulate nutrient transactions between sheep camps and the rest of the paddock. Net nutrient or alkalinity deposition in camps is treated as export from the paddock. Nitrate losses from camp areas could have added up to 8.4 kg N ha\(^{-1}\) year\(^{-1}\) to the size of the nitrate-leaching term recorded for the simulations.

Helyar and Porter [4] estimated that nitrate leaching added 1.4 kmol H\(^+\) ha\(^{-1}\) year\(^{-1}\) to the soil acid budget, almost twice the rate given by the simulation. Helyar and Porter [4] determined the acidification due to nitrate leaching indirectly as the component of acid addition that could not otherwise be accounted for (i.e., the retrospective application of the model as discussed in the introduction to this chapter). Because the total acidification rate was determined by pH change and pH buffer capacity, the estimate of the nitrate leaching term by this method depends directly upon the estimates of the carbon cycle terms.

6.5 Soil pH Profile Development

Soil pH profiles measured by Bromfield et al. [21] as well as pH profiles simulated by the GRAZPLAN soil acidity model for 26 and 55 years are given in Fig. 11. In the first 26 years of the run, both the total acidification and the distribution of pH within the soil profile lie within the range of the measured pH profiles for 26-year-old pastures (Fig. 11, profiles C, D, and E). The simulated pH profile for 1980 should be most comparable to measured profile H because the pH buffer capacity, the depth of the A horizon, and other factors used in the simulation were derived from data for this profile. However, the ranges of pH values at each depth across all three profiles (F, G, and H) probably give a more realistic target for comparisons as they give some idea of the variance that might be expected in acidified soil profiles. Total acidification after 55 years was similar to that calculated from the measured pH profiles. The simulation gave a substantial decline in soil pH in all soil layers. However, the change in pH of the 0 to 30-cm layer was underestimated, whereas a large amount of protons went into the 60- to 70-cm soil layer. The balance between alkalinizing and acidifying processes determines the net acid addition in each soil layer. The main acidifying processes are net proton excretion by the roots due to excess cation and ammonium uptake and proton generation due to nitrification of ammonium. Because the proton-generating processes in the nitrogen cycle are restricted to the upper soil layers and leaching of protons and aluminum is limited above pH 4, the distribution of the excess cation uptake effects is clearly a significant factor for the distribution of acidity in the subsoil layers. There is no clear experimental basis—in either the field or laboratory—for modeling the distribution of excess cation uptake across a root system, so a number of alternative strategies were explored (data not shown). For instance, excess cation uptake was distributed according to the distribution of nitrate uptake, the distribution of root mass, or the distribution of root tips. All failed to reproduce the observed soil pH profiles. The best solution was to distribute the hy-
drogen ion excretion due to excess cation uptake according to the distribution of root mass but modified by dependence on soil pH as described earlier. This has produced sensible results in a situation where the subsoil has acidified strongly. However, the restriction on excess cation uptake needed to obtain a reasonable pH distribution was greater than would be expected from the physiology of cation uptake alone [50]. We presume that there is not only a physiological effect of pH on excess cation uptake but in addition poor availability of cations [102] and toxic effects on root and root hair development in the acid soil layers [103]. The current logic of distributing proton excretion due to excess cation uptake provides an interim solution, and further work is required.

6.6 Conclusions: GRAZPLAN

Modeling of soil acidification under extensive grazing is particularly challenging because the phosphorus input drives carbon and nitrogen cycle acidification through several intermediate steps, e.g., nitrogen fixation by clover and nutrient redistribution by the grazing animals. Nevertheless, the GRAZPLAN soil acidity model was used successfully to simulate the impact of subterranean clover–based pasture on the soil pH profile development over a period of 55 years.

The work has identified areas where new knowledge is required for further progress in simulation of soil acidity. In particular, we are examining aspects of phosphate sorption, phosphate fixation, plant availability of phosphorus, and soil organic matter turnover in relation to plant productivity. In the present simulation, these factors were controlled. For instance, the phosphate sorption characteristic of the soil was set on the basis of results from a grazed fertilizer trial in progress on a similar soil, while rates of soil organic matter turnover were set to mimic the accumulation of organic nitrogen and phosphorus reported by Williams [99]. This allowed us to concentrate on issues that affected the generation and distribution of soil acidity under a pasture system. Simulation of the pH profile data reported by Bromfield et al. [21] revealed that two areas of the soil acidity model in particular require further examination: (1) the spatial distribution of excess cation uptake and proton excretion along root systems in soil and (2) the interaction with soil pH and the characteristics of urine deposits on grazed pastures and the associated nitrogen dynamics under urine patches. The interim solutions to both of these problems in the model have provided working hypotheses that will form the basis of further experiments. This case study shows that the integration of experimental and modeling approaches can be used synergistically to further our understanding of biological and chemical processes underlying agricultural systems.

7 CONCLUDING REMARKS

The implementation of the Helyar and Porter proton budget calculations in two agricultural systems models improves on the manual application of the framework
and presents more opportunities for analysis of soil acidification in agricultural systems. When properly parameterized, the two models described in this chapter are powerful tools for interpreting and extrapolating experimental data. As illustrated in the APSIM-SoilpH case study, use of the model for extrapolations in time can put the results and conditions of a short-term experimental study in perspective. When considering, for example, the amount of nitrate leaching measured in a single year, it goes beyond a simple comparison of seasonal rainfall with the long-term average by giving an integrative analysis of the effect of timing of rainfall relative to nitrogen uptake by the crop and management actions such as fertilization. Similarly, in the second case study the GRAZPLAN soil acidity model allows an analysis of processes occurring between experimental sampling dates, such as the nonlinear increase in total soil nitrogen.

Although the simulations presented in the case studies do not allow complete verification of all aspects of the models’ performance, they give sufficient confidence that the models describe the key proton-producing and proton-consuming processes well and are able to describe the pH profile development over time. In preparing the case study examples, we found, however, that accurate description of carbon and nitrogen dynamics is much more critical for modeling soil acidification than for simulating crop production or simulating drainage and nitrate leaching below the root zone. Some processes are currently not well defined due to lack of detailed experimental data, e.g., surface residue breakdown, below-ground fresh organic matter inputs (amount and C/N ratio of roots), and nutrient redistribution by grazing animals. Obviously, more work in these areas is required, preferably through well-defined experiments in conjunction with model development to ensure that the right data are collected.

This study stresses that the models are only as good as the science underpinning them and the inputs provided. How critical uncertainties about the process and input are generally depends on the type of application. Requirements for a qualitative “what-if” analysis are much less stringent than for a quantitative simulation of site-specific conditions.

Two types of model applications that are likely to become more and more important in the years ahead are not illustrated here, namely the use of models in the design of sustainable agricultural production systems and the use of models to support environmentally responsible and economically viable management decisions. Both APSIM-SoilpH and the GRAZPLAN soil acidity model provide opportunities in this area to analyze options for amelioration of soil acidity and to assist in management that will minimize soil acidification.

ACKNOWLEDGMENTS

We would like to thank Warren Bond, Mark Conyers, Perry Dolling, Neil Huth, Brian Keating, Andrew Noble, Roland Poss, Peter Randall, and Chris Smith for
many helpful discussions. Ian Johnson, Jim Scott, and Graeme Blair are acknowledged for their early work on formulation of the nutrient routines and the acidity model in NutriAce. Stephen Braithwaite is acknowledged for his work on an earlier version of SoilpH. We would also like to thank Frank Dunin, Roland Poss, Chris Smith, John Angus, and staff for the extensive data set collected at the CSU site (case study 1). The Vincent Fairfax Family Foundation supported this work through a fellowship to Dr. J. Braschkat. The work was further funded in part by CSIRO and the Land and Water Resources Research and Development Corporation.

REFERENCES


81. P Kauppi, J Kamari, M Posch, L Kauppi, E Matzner. Acidification of forest soils:


Using Geographic Information Systems (GISs) in Soil Acidification Risk Assessments

Patricia A. Hill
Department of Agriculture Western Australia, Ravensthorpe, Australia

1 INTRODUCTION

Risk is the probability that a hazard will become a problem [1]. In risk assessment, it is usual for risk criteria to be formally identified (e.g., Bui et al. [1]). First, it is necessary to determine what hazards contribute to the risk of the problem occurring. Second, criteria that need to be evaluated in order to determine the risk have to be established. Finally, it is necessary to ascertain at what level the hazard will become a problem.

The factors that contribute to the hazard of soil acidification include the initial soil pH, the soil pH buffering capacity, and the acidification rate [2]. Equation (1) can be used to estimate the number of years required for a soil to reach a critical pH value below which production losses are likely [2].

\[
\text{Time} = \frac{(\text{pH} - \text{pH}_{\text{crit}}) \times (\text{pH B.C.})}{\text{A.R.}}
\]

(1)

where

- \text{time} = \text{the number of years it will take for the soil to reach the critical pH}
pH = the current pH of the soil measured in 1:5 soil/0.01 M CaCl₂
pH B.C. = the buffer capacity of the soil in kg lime (ha⁻¹ 10-cm depth) year⁻¹
A.R. = the acidification rate in kg lime (ha⁻¹ 10-cm depth) year⁻¹
pHₜᵣᵢₜᵢ = the critical pHₜᵣᵢₜᵢ below which production losses are likely

In soil acidification risk assessments, as with most agricultural risk assessments, a “problem” occurs when productivity, or the sustainability of productivity, is affected. This happens when soil pH drops below a critical pH level. Identifying areas that are at high risk of soil acidification is achieved through determining the number of years until critical pH is reached, given the value of each of the contributing risk factors at any geographic location within the study area.

2 ACIDIFICATION RISK ASSESSMENTS

The expected number of years until a given critical pH is reached enables acidification risk predictions to be made by identifying the bracket within which the number of years falls. For example, a high-risk area is expected to reach critical pH in less than 15 years, a moderate-risk area in less than 30, and a low-risk area is not expected to acidify to critical pH within 30 years [3]. Where enough data are available, it is possible for maps to be created to represent the categories spatially [2].

Unlike assessment of acid sulfate soils [4] and salinization risks [1], it is not possible to use remotely sensed data to infer geomorphic features that are generally associated with areas with high risk of acidification using digital elevation models. The factors that contribute to agriculturally significant soil acidification are necessarily measured using soil surveys. Hence, soil surveys will always form a part of soil acidification risk assessments.

2.1 Initial Soil pH and Critical Soil pH

Management of acid agricultural soils involves increasing the soil pH to the point where economically significant decreases in plant production are avoided, usually within the economically significant pH range of 4 to 7 where soils are less well buffered [5,6]. Acidification forecasts and predictions of lime application requirement are also restricted to this range because alkaline soils are affected minimally as a result of strong buffering by carbonates and acid soils by the buffering of aluminum hydrous oxides [7].

The Al³⁺ ion is a major constituent of mineral soils, where it is present in a wide array of primary and secondary minerals [8]. It is generally considered to be the main aluminum ion that is toxic to plants, and it increases in concentration in soil solution below pH 5.5 [8–10]. Aluminum concentrations in soil that have been shown to affect plant growth vary according to plant susceptibility; critical
pH values have been determined for categories of susceptibility of plant species to Al toxicity [11–13].

2.2 Acidification Rate

In simulating future soil acidification, it is necessary to determine the acidification rate, which is a factor of net acid addition to, and loss of alkalinity from, the soil system. Acidification rates are related to land use, and increases in acidification rates compared with undisturbed systems are a characteristic of southern Australian agricultural systems [14]. Determining current acidification rates is imperative for facilitation of corrective action because prolonged periods of high acidification rates may result in subsoil acidification. Ameliorating subsoil acidification is not always economically viable [14].

Acidification rates have been determined historically from the change in pH over a given time period [Eq. (2)] [15,16]. This may be done for the same site over time or for adjacent sites with different land uses (fenceline surveys) [14].

\[
\text{Acidification rate} = \frac{\Delta \text{pH}}{\text{year} \times (\text{pH B.C.)}}
\]  

Acid addition rates are related to the production system, fertilizer and acid inputs, soil texture, organic matter content (pH buffering capacity), time since clearing, annual rainfall, and initial pH [14,15,17].

Time since clearing has been shown to influence the acidification rate, with rates observed ranging from \(-0.39\) kmol H\(^+\) ha\(^{-1}\) per year for 8 years from clearing to \(1.58\) kmol H\(^+\) ha\(^{-1}\) per year 40 years from clearing [18]. Dolling and Porter [19] reported similar observations, with acidification rates from \(0.19\) to \(0.23\) kmol H\(^+\) ha\(^{-1}\) per year from 12 to 74 years since clearing.

The average annual rainfall determines crop yields and hence removal of alkaline plant produce from the paddock, as well as the degree to which nitrate is leached. For example, acidification rates under continuous wheat rotations are directly related to rainfall [20]. Also, leguminous crops produce greater soil acidification rates than cereal crops [21].

2.3 Buffer Capacity

The buffer capacity of soils refers to the impact that addition of either acid or base has on the soil pH; i.e., the buffer capacity is the in situ titration curve of the soil [5,22]. Soil pH buffer capacity can be measured in the laboratory [22,23]; however, it is rarely measured for soils because of practical problems associated with buffer capacity analyses on a large scale. Buffer capacity may also be predicted from other soil properties that are readily measured or observed, such as organic matter and clay content [17,24,25]. Equations involving both organic carbon and clay content have been used in Queensland [17] and Western Australia [14].
Clay has been shown to have a weak buffer capacity relative to organic matter [26]. In fact, the buffering contribution of organic matter may be in the order of 10 times that of clay. Values for organic matter have been reported as being between 4 and 10 kmol H$^+$ ha$^{-1}$ per pH unit and per 10 g organic matter kg$^{-1}$ soil and clay buffer capacity as being between 0.45 and 0.62 kmol H$^+$ ha$^{-1}$ per pH unit and per % clay [5]. Helyar et al. [14] state that for Australian soils values of 4.2 kmol H$^+$ ha$^{-1}$ per pH unit or 10 g organic matter kg$^{-1}$ soil and 2 kmol H$^+$ ha$^{-1}$ per pH unit and per % clay should be used. Simple equations have been determined that relate buffer capacity to organic matter based on the assumption that all organic matter has an equal buffer capacity and that there is enough organic matter to influence strongly the soil buffer capacity [3].

Curtin and Rostad [26] concluded that in situations where clays are weakly buffered due to mineralogy (e.g., kaolin-dominated clay) and where organic matter is low, soils would be susceptible to acidification even when clay content is relatively high. As significant differences in pH buffer capacity between soil groups have been observed [17], it is likely that buffer capacity calculations based on soil properties will be region specific.

In Western Australia, regional mapping has shown the existence of a generally uniform pattern of soils and landforms, referred to as a catena or toposequence [27]. Local geology and soil formation determine soil characteristics, in particular clay mineralogy and soil texture, that in part determine the buffer capacity of the soil. Hence, it seems reasonable to expect to be able to predict the comparative buffer capacities of disparate soils within a region. The buffer capacity may also be inferred from the relationship between landform and soil texture for any given region; e.g., soils on ridges may be associated with a buffer capacity different from that of soils that are found on slopes.

3 GEOGRAPHIC INFORMATION SYSTEMS

The ability of a geographic information system (GIS) to handle geographic data in digital form enables diverse sets of spatial data to be captured, stored, manipulated, analyzed, and finally displayed [28]. There are two main data structures in GISs. Vector structures use points, lines, and polygons to represent the location and extent of features such as sample sites (points), fencelines (lines), and land use (polygons). Raster structures use a regular grid for which each cell has a value for any geographic variable, for example, soil clay content or pH.

Soil maps frequently form a component of spatial analyses related to agriculture. In particular, the development of precision agriculture has seen the associated evolution of GISs and methodology capable of producing soil maps with some accuracy. The importance of soil mapping is derived from the fact that soil properties control a range of processes that have significant consequences for agricultural and environmental management [29].
The final soil maps produced have historically relied on the ability of the soil surveyor to infer features of soil variation from readily observable attributes [29]. This process is based on the assumption that development of soil characteristics is reliant on five principal soil-forming factors and processes, these being parent material, landform, time, climate, and biological activity [30]. On the other hand, the soil map may be created within the GIS environment using a raster data structure; this method relies less on user interpretation than on mathematical relationships [31]. The best method for producing a soil map is one that uses conceptual models devised by a soil scientist and is complemented by the objectivity of GIS.

Cook et al. [29] introduced a rule-based approach to mapping soil properties. Prediction of an unquantified soil characteristic at point \( x \) is made according to the value of other quantified characteristics that are known to influence the unquantified characteristic [29]. As discussed previously, it has been shown that clay and organic matter contents are determinants of soil buffer capacity. Hence, knowing the value of the predictor variables (in this example clay and organic matter contents), we are able to make some assumptions about the unquantified characteristic, in this case the buffer capacity, at any unvisited site.

This method is further developed by weighting the evidence according to its perceived sufficiency or necessity [29]. It was shown earlier that the buffer capacity for any given point \( x \) may be estimated on the basis of organic matter content and clay content. Weighting the influencing characteristics according to a tested equation can provide accurate predictions about the value of the buffer capacity at an untested site using values of characteristics that are readily observed. That is, buffer capacity may be spatially estimated using an experimentally determined equation.

### 3.1 Spatial Interpolation of Soil Properties

Representation of spatial continuity is possible by depicting the surface continuously to show gradual variations in soil properties [32]. This may be achieved by interpolating values of variables at unvisited sites in the GIS on a cell-by-cell basis in a raster environment.

The resultant map using interpolation is considered accurate compared with conventional chloropleth maps in some situations. For example, Burrough [33] showed that mapping the clay content of the topsoil for an area in Italy using conventional mapping gave an average 39% variance for clay content. Using interpolation produced a map for which the error variances did not exceed 21% clay content, which in effect was 2.5 times better than the chloropleth map [33].

Powell and Ahern [4] have delineated risk factors using a vector data structure in assessing the risk of acid sulfate soils. Moore [2] has also developed a method of producing soil acidification risk maps using GISs in which an acidification risk value was associated with each soil type, producing risk maps that
showed discrete (and hence artificial) boundaries. This problem has been overcome by interpolating the soil properties that are shown to affect soil acidification risk, resulting in continuous surfaces that more closely represent reality [34]. The following steps are applied to a data set in order to produce continuous soil acidification risk maps:

1. Development of a soils map and association of the various soil types with bulk density values
2. Acquisition of point observations of soil pH, organic matter, exchangeable aluminum content, clay content, and buffer capacity
3. Determination of a relationship between soil buffer capacity and the other soil properties
4. Interpolation of grids of the factors in step 2 that were used in step 3 and a grid of initial pH
5. Use of raster algorithms to weight the various factors according to the relationship in step 3
6. Incorporation of the initial pH grid with the buffer capacity to produce acidification risk maps and lime requirement maps [34]

4 A CASE STUDY—THE WEST RIVER CATCHMENT*

4.1 Study Area

The West River Catchment is 43 km west of Ravensthorpe, 30 km from the south coast of Western Australia, and covers approximately 30,000 hectares (Fig. 1). The area receives an average rainfall of 370 mm at the north of the catchment and 420 mm to the south [35]. The main produce of the area includes wheat, barley, lupins, canola, sheep, and cattle.

The West River joins the Phillips River within the Fitzgerald River National Park, and the Phillips River drains into the Southern Ocean 20 km west of Hopetoun. The catchment is separated from the ancient internal drainage lines and salt lake chains by the Jarrahwood axis [36]. The catchment consists of a shallow, narrow valley, 15 km wide, with the highest point of the catchment being 350 m above sea level and the lowest 240 m above sea level.

The higher regions of the catchment are mainly colluvium derived from granitoid rocks including granitoid gneiss; the flats are undulating, reworked sandplain deposits and peneplain remnants. Drainage lines contain silcretes formed in regolith over granitoid rock, with some biotite monzogranite and granodiorite coinciding with the river [37]. Influencing the soil pattern across the landscape are the full laterite profiles that may be observed in a transect from the higher regions into

* From Hill [34].
FIGURE 1  Location of the West River Catchment, Western Australia.
the drainage lines. Laterite breakaways of the peneplain are actively eroding [35]. Short et al. [35] observed that the present soils have formed primarily on the pallid zone clays, hence resulting in primarily duplex soils. It is also noted that there are many dolerite dykes throughout the southern part of the catchment.

4.2 Collection of Case Study Data

A soil survey was conducted in April 1999 in order to collect soil samples from as many disparate soil types as possible. Sites were visited according to their landform, delineated on the basis of predetermined soil mapping units using aerial photographs. Actual location was determined using global positioning system (GPS).

From each site, topsoil and subsoil samples were taken from the profiles. Soil samples were analyzed for color, pH, extractable aluminum, soil pH buffering capacity, texture (clay content), gravel content, and organic matter. Loamy sand accounted for 53% of the total area in the topsoil, while 75% of the subsoil was clay or sandy clay. Upland (plateau) soils were characterized by shallow and sandy gravels or sand over a gravel/loam matrix. Slope soils were generally duplex soils, characterized by light-colored (gray) sands over gray or brown clays.

4.3 Initial and Critical Soil pH

Fifty-three percent of samples fell between pH 4.5 and 5.5. A significant systematic relationship between the extractable aluminum and pH was observed [Eq. (3); Fig. 2].

![Figure 2](image)

**Figure 2** Relationship between the logarithm of CaCl₂-extractable aluminum and pH in 0.01 M CaCl₂ for 120 soil samples taken from the topsoil and the subsoil of profiles in the West River Catchment.
Critical pH values were chosen on the basis of this relationship.

4.4 Buffer Capacity

Average carbon content for topsoil was 14 g kg\(^{-1}\), 3.5 times higher than in the subsoil (4 g kg\(^{-1}\)). Both values are considered to be medium for their respective depths [38] (Fig. 3). For the average “fines” (<2 mm particle size), buffer capacity was 0.73 cmol H\(^+\) kg\(^{-1}\) soil per pH unit (207 kmol H\(^+\) per ha and per pH unit using bulk density values).

The factors found to contribute to buffer capacity predictions included the clay proportion and the organic matter content; however, the best relationships were obtained when the topsoil samples were separated from subsoil samples. The prediction of buffer capacity for the <2 mm fraction of the topsoil was significantly related to both the organic matter content and the clay content [Eq. (4)]

\[
\text{pH B.C.} = 0.131 + 0.0161(\% \text{ clay}) \\
+ 0.394 \left( \frac{\text{g organic carbon per kg soil}}{10} \right) \quad R^2 = 0.86 \tag{4}
\]

The buffer capacity for the subsoil was best predicted taking into account only the proportion of clay [Eq. (5)].

\[
\text{pH B.C.} = 0.39 - 0.021(\% \text{ clay}) + 0.00091(\% \text{ clay})^2 \quad R^2 = 0.97 \tag{5}
\]
5 APPLICATION OF GIS TO THE CASE STUDY DATA

The spatial analysis was conducted using ARC/INFO, version 7.1.3 (ESRI). All steps were written into Arc Macro Language applications (AMLs) so that the process was fully automated. The AMLs were linked to a graphic user interface menu bar, allowing simple completion of simulations.

5.1 pH Data

The GPS coordinates of sites visited were associated with the corresponding pH data in tables in ArcView (ESRI). The entries for each separate depth (topsoil and subsoil) were selected from all entries in tables in ARC/INFO and were used to create coverages for each depth. These coverages were then used to create an interpolated pH grid for each depth using inverse distance weighting (IDW) in GRID.

5.2 Buffer Capacity

Several steps were required in order to create the buffer capacity grids for the topsoil and subsoil across the catchment.

1. *Determination of the predictors for buffer capacity:* the relationship between buffer capacity and other soil factors, as given previously [Eqs. (4) and (5)].
2. *Clay content:* interpolation of a clay grid using the point texture values was used to determine the clay content across the catchment. This was chosen in preference to creating a soil texture map and converting it into a grid because soil texture boundaries are an arbitrary delineation of a continuous surface, which could not be taken into account using the discrete delineation of polygons. An item “clay” was added to each depth’s polygon attribute table (PAT) and was given a value according to the soil texture (derived from Needham et al. [39]). The clay point coverage was then interpolated into a grid using IDW in GRID. This allowed continuous representation of the surface so that further grids could be calculated using raster algorithms.
3. *Gravel grid:* a gravel grid was created from the “gravel” item in each depth coverage PAT, using IDW with the same cell size and map extent as for the previous grid.
4. *Carbon grid:* a carbon grid was created for the topsoil. An item “carbon” was added to the topsoil PAT and given a value according to the average value for the land use at that site. This item was then converted into a grid.
5. *Fines buffer capacity grid:* a buffer capacity grid was created for the <2 mm fraction (“fines”) of the soil in each depth (topsoil and subsoil).
Equation (4) was used to create the fines buffer capacity grid for the topsoil and Eq. (5) for the subsoil.

6. **Total buffer capacity grid:** the total buffer capacity grid was then determined using Eq. (6a) [in terms of raster algorithms, Eq. (6b)], which gave the buffer capacity in cmol H⁻¹ kg⁻¹ soil (pH unit)⁻¹.

\[
pH \text{ B.C.}_\text{Total} = \left[ \text{B.C.}_{\text{Gravel}} \times (\% \text{ gravel}) \right] + \left[ \text{B.C.}_{\text{fines}} \times (\% \text{ fines}) \right]
\]

\[
\text{totbuff} = \left[ 0.144 \times \left( \frac{\text{intgrav}}{100} \right) \right] \left[ \text{finebuff} \times \left( 1 - \frac{\text{intgrav}}{100} \right) \right]
\]

In Eq. (6a), total buffer capacity (B.C.\text{Total}) is determined by proportion of gravel multiplied by its buffer capacity in cmol H⁻¹ kg⁻¹ soil (pH unit)⁻¹ (B.C.\text{Gravel}) plus the <2 mm fraction multiplied by the fines buffer capacity value (B.C.\text{fines}). In Eq. (6b), Eq. (6a) is converted into a raster algorithm, where totbuff is the total buffer capacity created, intgrav is the interpolated gravel grid, finebuff is the fines buffer capacity grid, and 0.144 is the observed average buffer capacity of ferruginous gravel in cmol H⁻¹ kg⁻¹ soil (pH unit)⁻¹.

7. **Conversion of buffer capacity grid:** a total buffer capacity grid was created in units of kg lime ha⁻¹ (pH unit)⁻¹ so that acidification risk and lime requirements could be calculated. An item BD (bulk density) was added to the texture coverage PAT and given values in t m⁻³ on the basis of those given in Needham et al. [39]. The texture polygon coverages were then converted into grids using the BD item.

Buffer capacity values were converted to kmol H⁺ (ha⁻¹ 10-cm layer) (pH unit)⁻¹ using the conversion equation of Moore et al. [3] [Eq. (7a)], where pH B.C. is the soil pH buffer capacity and BD is the bulk density grid. Conversion into a raster algorithm gives Eq. (7b).

\[
\text{pH B.C.}_{\text{(kg lime per ha 10-cm layer per pH unit)}} = \text{pH B.C.}_{\text{(cmol H⁺ per kg soil per pH unit)}} \times \frac{500}{\text{BD}}
\]

\[
\text{B.C.}_{\text{converted}} = \left[ \left( \frac{\% \text{ gravel}}{100} \right) \left( \text{B.C.}_{\text{gravel}} \right) \right] + \left[ \left( 1 - \frac{\% \text{ gravel}}{100} \right) \left( \text{B.C.}_{\text{fines}} \right) \times \frac{500}{\text{BD}} \right]
\]

where the total buffer capacity grid in kg lime ha⁻¹ (pH unit)⁻¹ (B.C.\text{converted}) is created using the gravel grid (% gravel), the gravel buffer capacity (B.C.\text{gravel} =
0.144), the fines buffer capacity (B.C.fines, in cmol H$^{+}$ kg$^{-1}$ soil (pH unit)$^{-1}$, and the bulk density grid (BD).

The processes just described are summarized in Fig. 4.

Buffer capacity of surface soil is generally uniform across the catchment, being between 200 and 400 kg lime ha$^{-1}$ (pH unit)$^{-1}$. The subsoil shows more variation in buffer capacity, with most of the east side of the catchment having a buffer capacity between 100 and 300 kg lime ha$^{-1}$ (pH unit)$^{-1}$ and the west side between 0 and 200 kg lime ha$^{-1}$ (pH unit)$^{-1}$.

5.3 Years Until Critical pH Is Expected to Be Reached

The predicted number of years until critical pH is expected to be reached was determined using Eq. (1) [3]. Acidification rates were chosen from the data pre-
sented in the literature. These values were converted into kg lime ha\(^{-1}\) year\(^{-1}\) so that they could be used in Eq. (1). This was achieved using the assumption that 1 mole of CaCO\(_3\) neutralizes 2 moles of H\(^+\) in the soil (G. Moore, personal communication, 1999).

Maps of the number of years until critical pH is expected to be reached were created for critical pH values of 4.05, 4.13, and 4.55. These values correspond to the pH at which extractable soil aluminum reaches critical concentration for tolerant ([Al] = 45 μM), sensitive ([Al] = 37 μM), and highly sensitive ([Al] = 15 μM) plants, respectively, based on the relationship shown in Fig. 2. Acidification rate values were chosen to cover a wide range of acidification rates from the literature, including 2, 4, 7, 10, and 20 kg lime ha\(^{-1}\) year\(^{-1}\) (this refers to the lime equivalent removed from the soil system for the 10-cm layer, dependent on crop type).

5.4 Acidification Risk

Acidification risk grids were created using several of the “years until critical” grids (created as described earlier). In this way, risk grids could be created for any given scenario determined in the years until critical component. Each raster cell of the grid was given a value according to the years required to reach the critical soil pH value for each raster cell of the critical grid. Cells with a value of 3 or less were given an acidification risk value of 1 (imminent risk), cells with a value between 3 and 15 were given an acidification risk of 2 (high risk), cells with a value between 15 and 30 were given a value of 3 (moderate risk), and above 30, cells were given a risk value of 4 (low risk).

The acidification risk maps show that for the topsoil, there are three areas that are at the highest risk of acidification. These areas are along the highway, at the southeast of the catchment, and a small area along the northern boundary of the catchment. For the subsoil, the high-risk areas are scattered throughout the catchment but trend north–south through the center of the catchment (Fig. 1).

6 USING GIS IN ACIDIFICATION RISK ASSESSMENT—ADVANTAGES AND DISADVANTAGES

Due to the degree of erosion of the West River Catchment, the clay minerals, derived from granitoid rock and granitoid gneiss, are likely to be highly weathered [37]. It is therefore assumed that, like most soil clays in Western Australia, the clays in West River soils are predominantly kaolinic (T. Overheu, personal communication, 1999) [40]. Because kaolinic clays have low cation exchange capacity compared with other clays and consequently a relatively low buffer capacity [41], most of the catchment is at high risk of soil acidification.

Ascertaining the nature of the soil catena across the landscape can allow general statements to be made about the acidification risk of a region. In particu-
Soils formed on lateritic profiles are inherently low in bases [42] and high in kaolin and/or aluminum hydroxide [43]. This has significance for acidification studies due to the toxicity of aluminum at low pH. Furthermore, because buffering capacity was shown to be closely related to clay content, a conceptual framework may be established such that land managers may prioritize lime application to landforms known to possess a particular suite of acidification-susceptible soils.

Accuracy of soil acidification assessments is limited by the strength of the relationships used to predict the soil pH buffer capacity [23]. In the case study data, buffer capacity was predicted with a high degree of confidence. This may be attributed to a large sample size and geographically confined nature of the study—soils and land use were fairly uniform across the catchment.

Soil pH buffer capacity predictions are calculated from the rate of pH change with addition of acid or base in the range where the slope is greatest. This was determined as being between pH 4 and 6.5, with rate of pH change diminishing outside this range. Hence, predictions of pH change with the addition of lime or acid will be restricted to this range. Due to the high buffering of soils below pH 4 by aluminum hydrous oxides and kaolinite, it is unlikely that soil pH will decline much below 4 [7]. Predictions of pH decline will therefore be overestimated for soils with pH below 4, resulting in pH predictions for acid soils that are too low.

In contrast to findings by Curtin and Rostad [26], organic matter was shown to have a significant influence over buffer capacity only in the surface soil. On the other hand, including clay content improved the accuracy of the buffer capacity prediction equation for both the topsoil and the subsoil. Extractable aluminum has also been used to predict pH buffering capacity, e.g., in Queensland soils [44]; however, aluminum was not significantly related to buffering capacity in this study. This is probably because buffer capacity was measured between pH 4 and 6.5, where neutralization of exchangeable aluminum is not an important factor in buffering change in soil pH [14]. In this pH range, the main buffering reactions are proton dissociation and association from pH-dependent groups on the edges of clay minerals and oxides and from the carboxyl, hydroxyl, and phenolic groups of organic matter [14].

The dominant role of organic matter in soil buffering may be due to its high affinity for acidic metal cations [45]. Humic substances form relatively stable complexes with acidic cations, e.g., Al$^{3+}$, both in soil solution and adsorbed to the surface of clay minerals [45]. On addition of protons to the soil, organic matter plays a role in providing adsorption sites for fast reaction [25]. Organic matter source and degree of humification are thought to affect the buffer potential per unit mass of organic matter, and it is noted that surface organic matter was generally not highly decomposed, possibly influencing the number of reactive sites in the organic matter. Hence, although organic matter quantity is high in soil under cereal stubble, its quality may predicate that the buffer capacity for each unit of
organic matter is overestimated. The equation assumes that all organic matter has equal buffer capacity, which is unlikely.

Organic matter content in the subsoil was probably not sufficient to influence the buffer capacity. Also, inclusion of organic matter for the subsoil was not possible because there was no surrogate measure that could be interpolated to predict accurately organic matter content across the catchment. That is, unlike the topsoil, differences in organic matter content for each land use were not systematic. It is recommended that land managers acquire data on soil organic carbon content in order to determine the buffer capacity for topsoil.

The significant influence of clay is probably related to the high clay content in the subsoil and is despite the low chemical activity of kaolin group minerals. The average buffer capacity for the catchment is low compared with predicted buffer capacity values using the equations given in Moore et al. [3] and similar clay and organic matter content values. It is concluded that the clays in the West River catchment are poorly buffered against pH change, even though clay is the most significant source of active sites within the pH range 4 to 6.5.

The acidification risk equation used in the case study relies on the accuracy of soil pH buffering capacity and acidification rate values. The equation is simplistic, assuming that the in situ buffer capacity is equivalent to that observed in the laboratory. It also assumes that buffer capacity remains constant with time, which is unlikely because organic carbon contents are dynamic, increasing and decreasing in relation to land management practices. Predictions of acidification risk are therefore likely to be more accurate for the subsoil because clay content will remain relatively constant with time. Using a constant acidification rate also ignores the influence of variable rainfall and land use across the catchment. It is expected that land managers will use a value that best represents the acidification rate for their situation, based on published data. When more accurate acidification risk equations become available, they will be readily incorporated into the GIS.

Acidification rate data are scarce, particularly for the southern coastal area of Western Australia. Acidification rates are rarely determined for separate depths, and in the absence of such data and for the purpose of this study, the acidification rate values were chosen to cover a wide range. Obtaining data for the actual acidification rate for sites within the catchment may allow more appropriate values to be chosen because acidification rates are affected by soil properties, climate, land use, and land management practices [14,15,17].

The clear relationship between pH and extractable aluminium means that critical pH values, based on the pH at which aluminium reaches a critical concentration, may be determined with a high level of confidence. A good relationship between pH and extractable aluminium is expected in the absence of organic matter and low concentrations of inorganic compounds that adsorb aluminium [46]. This is further evidence that the clays and organic matter in the catchment are relatively unreactive, having few adsorption sites to either buffer against pH change...
or adsorb aluminum. Choosing critical pH values on the basis of critical soil solution aluminum concentrations for plants ignores the effects on other factors, e.g., soil biological activity.

The acidification assessment is a time-consuming process; however, writing the separate processes into AMLs will mean that future assessments are expedited, and a similar soil acidification assessment could be completed in a very short period of time, depending on the scale of the study. The process also required a system capable of analyzing and storing very large files, so is probably not suited to small or inefficient computers. Also, the software used for this assessment (ARC/INFO) is a package that is not readily available to land managers. Aside from the computational requirement, the initial assessment relied on advanced GIS knowledge. However, linking the AMLs to a graphic user interface in the GIS environment will allow users with little or no GIS knowledge to perform an equivalent study.

Using inverse distance weighting was a means of interpolating the grids while returning the exact value at the sample sites. The resultant grids show maxima and minima in unrealistic spatial patterns, such that barriers to spatial spread are not taken into account. Also, IDW does not take into account spatial variability of the regionalized variable [47]. It may be possible to develop associations between soil mapping units and other characteristics within the GIS. This would enable the use of mapping units to act as barriers to the spatial spread of the variables and also ensure that only values obtained for the same mapping unit were considered when interpolating the surface. For example, averages of the clay buffer capacity would have been separated into the mapping unit from which the original observation was made—upper slope values would have been interpolated separately from lower slope values and so on. This would allow a more accurate interpolation procedure to be used (such as kriging) to give superior results in terms of accuracy compared with inverse distance weighting.

It was not possible to use kriging in this case because the distance between sample sites was above the maximum allowable for that procedure [48]. Kriging uses the dependence between spatially located observations represented by a variogram model and weighted according to the spatial dependence between observations [47]. In regions where the soil–landscape relationship is well defined, kriging will greatly improve the accuracy of soil acidification risk assessments. It is probably not suitable for small-scale studies because derivation of semivariograms for spatial dependence of soil properties is a complex process over large areas.

7 CONCLUSIONS

The acidification component developed for ARC/INFO has the potential to be used by land managers for studies of any scale, particularly if the component is improved into a formal computer program. This component would provide a valu-
able basis for future work in developing a more accurate, complete, and efficient program for acidification risk assessments.

A very important application of this acidification risk assessment technique is in assisting land managers to identify areas that are at high risk of soil acidification because soil acidity is largely an “invisible” problem until the situation is critical. It is anticipated that the methodology developed here may be applied to soils in agricultural regions throughout the world for improving the way in which acid soils are managed. Furthermore, the process has also been developed to create lime recommendation maps as well as maps showing the predicted pH at any given number of years from the present.

Suitable methodology for using geographic information systems to perform spatial analysis on a soil acidification data set is now available. The methodology used is an appropriate framework for soil acidification assessments. In particular, GIS is well suited to storing the case study data, performing spatial analyses, and presenting the output.

ACKNOWLEDGMENTS

This chapter is based on honours research conducted under the supervision of Professor Bob Gilkes and Dr. Andrew Rate at the University of Western Australia. Partial funding was supplied by the Ravensthorpe Land Care District Committee (LCDC).

REFERENCES

6. KR Helyar, MK Conyers, AM Cowling. Reactions buffering pH in acid soils treated


1 INTRODUCTION

Soil properties vary on all scales of observation. Nevertheless, we think of soils predominantly in terms of homogeneous material. To think in this way might be justified for the agricultural soils that have been homogenized by plowing. Such simplifications are useful in developing concepts and models. However, only minimum tillage or no tillage is applied to a large portion of agricultural land, and for most forest ecosystems, homogenization by plowing has never been done. Moreover, in acidified soils burrowing and homogenizing animals, such as earthworms, diminish. It is therefore worthwhile to study the heterogeneity of soils.

Soil acidity limits plant growth. The release of Al into the soil solution as a result of proton buffering is suggested to have effects on root growth and nutrient uptake [1,2]. In water culture experiments, the ratios Ca/Al and Mg/Al, rather than the Al concentration itself, is an indicator of the root damage [2–5]. The significance of these ratios for root activity under field conditions, especially for mature trees, however, is still under discussion [6]. Nevertheless, the Ca/Al and Mg/Al ratios are often used to estimate the detrimental effects of soil acidification on trees and for the calculation of critical loads for acid deposition [6–8].
Aluminum inhibits Ca uptake by blocking Ca\(^{2+}\) channels in the plasma membrane [9] and Mg uptake by blocking the binding sites of transport proteins [10]. A high concentration of Mn\(^{2+}\) also inhibits Ca and particularly Mg uptake. On the other hand, the K uptake is not affected by Al or Mn [11,12].

The soil acidification of forest ecosystems has been dominated by anthropogenic atmospheric deposition in past decades, especially in the northern hemisphere [13,14]. However, in the last 15 years, the emission of SO\(_2\) and subsequently the deposition of H\(^+\) and SO\(_4^{2-}\) in forest ecosystems in Europe and Northern America have decreased substantially, but N deposition remains high [15–17].

Temporal and spatial variation in deposition as well as different filter properties of trees cause a heterogeneous pattern in soil input [18]. Connected with spatially different buffering and exchange capabilities, the spatial and temporal heterogeneity in soil properties emerges, leading to acidic “hot spots” as well as short-time bursts in H\(^+\) activity.

Two aspects of heterogeneity are focused on in this chapter: (1) the consequences of soil heterogeneity for representative sample collection and data interpretation and (2) the effects of soil heterogeneity and the acidic pattern on root and plant growth and calculation of critical loads.

2 CASE STUDIES

Some investigations have been done on spatial and temporal heterogeneity of soil solution chemistry in forest ecosystems [19–27]. However, the numbers of samples in these investigations were low or the investigations were carried out for only a short time.

For a long-term investigation of soil heterogeneity at different spatial scales, a catchment in southeast Germany was fitted out with the measurement equipment for deposition, soil solution, and runoff monitoring [18,28,29]. Results from these investigations and from a state soil investigation in Germany [30] are presented here as case studies.

2.1 Sites and Measurements

The Lehstenbach catchment covers 420 ha and is located in the Fichtelgebirge, a mountain range in northeast Bavaria (Germany). This area is characterized by yearly average temperatures of 6.0°C (1987 to 2000, minimum 4.1°C, maximum 7.2°C) and annual precipitation rates from 623 to 1270 mm (average 929 mm). The annual throughfall is 573 to 952 mm (average 727 mm) and the seepage 256 to 684 mm (average 489 mm). The altitude ranges from 700 to 877 m above sea level. Close to 90% of the catchment is covered by Norway spruce [*Picea abies* (L.) Karst.] with an average age of 50 years [31].
At the Lehstenbach catchment, the granite bedrock is deeply weathered and strongly heterogeneous down to 30 to 40 m in depth. Among the soils, dystric cambisols predominate. Peaty soils and bogs cover one third of the catchment. The catchment is drained by a dense and irregular network of brooks and ditches. The altitude of the catchment is 690 to 877 m above sea level. Mean annual precipitation is up to 1100 mm. Annual average temperature at the mountain top (1992 to 2000) is 5.7°C (minimum 4.0°C, maximum 6.7°C). Approximately 90% of the catchment is covered with a spruce forest.

For microscale investigations 60 microsuction cups and 45 microtensiometers, each 1 mm in diameter and 5 mm in length, were installed in one wall of a small soil pit on a systematic grid (2 cm × 2 cm) at the Coulissenhieb site. The installation covered a soil depth to about 20 cm and an area of 180 cm² in total, ranging from the upper A to the Bv horizon. Further details are given in Ref. 32.

Typical sampling volumes from the microsuction cups ranged from 0.05 to 1.5 mL of soil solution, with an average of 0.58 mL. Soil suction data were collected at a sampling rate of one per minute and condensed to a 10-minute average. The 48 soil matrix samples were taken in two areas of 8.5 cm². The horizontal and vertical spacing of the sampling was 15 mm. For the sampling, a stainless steel tube (sample volume about 2 cm³) was used.

At the Coulissenhieb, a part of the Lehstenbach catchment, mesoscale investigations were performed. The investigation site was 2.7 ha. Underneath a 140-year-old Norway spruce stand, understory vegetation was rather sparse, comprising Deschampsia flexuosa, Vaccinium myrtillus, and Calamagrostis villosa. Twenty throughfall samplers, five suction cups, and tensiometers at 20, 35, and 90 cm depth, respectively, were installed with 2 m distance along four lines. Throughfall samplers and suction cups were sampled twice weekly. The temporal resolution of tensiometers was 1 hour.

At the macroscale, water and element fluxes (bulk precipitation, throughfall, transpiration, evaporation, seepage, and catchment runoff) have been measured continuously at up to 10 plots in the catchment. Soil matrix potentials and soil water contents have been measured hourly. Soil solution, groundwater, springs, and brooks have been sampled fortnightly. Soil matrix has been studied intensively at six main study sites as well as at the catchment scale. For the determination of sorbed SO₄²⁻, soil samples were taken within the catchment on a systematic grid with a mesh distance of 300 m and with four replicates at each mesh intersection [33,34].

For the regional scale, data from the soil state survey (BZE [35]) from the German states Lower Saxony and Saxony were compiled.

Because timber increment data were not available for the Lehstenbach catchment, a comparison between the soil chemical data and the increment from the Solling site was performed. This site has similar stocking and a similar soil state. The Solling area is located in the southern part of Lower Saxony in north-
west Germany (51°45’ N, 9°34’ E). Mean temperature is 6.5°C and annual precipitation is 1088 mm year\(^{-1}\). The plot is located about 500 m above sea level and vegetated by a 117-year-old Norway spruce plantation. A detailed description of the plot has been given in Ref. 36.


### 2.2 Analytical Methods

Chemical analysis of soil solutions collected by the microsuction cups (Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\)) was done by capillary electrophoresis [37] and ion-sensitive field effect transistor (ISFET) pH measurements. The soil solution collected from the normal-sized suction cups as well as water samples were analyzed by ion chromatography (Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\)). The pH was measured with a glass electrode.

Chemical analyses of soil samples were carried out sequentially on initially 1-g samples. Soil suspensions were diluted to 10 cm\(^3\), shaken for 1 hour, and centrifuged. In the supernatant, SO\(_4^{2-}\) was measured by ion chromatography.

Desorbed SO\(_4^{2-}\) was determined at all scales by percolating field-moist samples with H\(_2\)O. The data were fitted nonlinearly to a modified Langmuir isotherm. Further details are given in Refs. 34 and 38.

### 2.3 Mathematical Methods and Modeling

Water fluxes in soil were calculated for each point by a numerical simulation model. The ion fluxes at each lysimeter were established by multiplying the simulated water fluxes by the ion concentrations on a fortnightly basis [18].

The model MAGIC (Model of Acidification of Groundwater in Catchments [39]) was employed to evaluate the effect of spatially different sorption/desorption isotherm parameters on long-term SO\(_4^{2-}\) dynamics prediction. The model describes cation exchange as an equilibrium reaction between the base cations (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\)) and Al. For details see Refs. 33 and 34.

The number of samples required to match the population average can be calculated if the desired statistical precision is fixed. The computations followed the equation [40]

\[
n_{\text{req}} = \frac{z_{\alpha}}{\bar{x} - \mu} \sigma^2
\]

where \(n_{\text{req}}\) is the minimal number of samples, \(z_{\alpha}\) the \(z\) value (1.96 for \(\alpha = 0.05\) was used here), \(\bar{x} - \mu\) the demanded precision, and \(\sigma\) the standard deviation of the population. In this case \(\sigma\) had to be estimated conservatively with \(\sigma = s\), where \(s\)
was the standard deviation of the sample. The precision $\bar{x} - \mu$ was fixed to $\pm 10\%$ of the corresponding fortnightly average, which can be seen as a moderate requirement. The computation required a normal distribution of the underlying data. This was tested by the $W$-statistic test [41,42] for each ion, each compartment, and each sampling date. The zero hypothesis, that the values are normally distributed, could not be rejected at the 99% significance level.

2.4 Results

2.4.1 Input, Soil, and Runoff Heterogeneity of Matter Fluxes

For the assessment of the soil heterogeneity, it is important to compare it with input and runoff heterogeneity. A considerable part of heterogeneity emerges from the trees as structural elements while combing out reactive gaseous constituents from the atmosphere (e.g., $\text{SO}_2$ and $\text{NO}_x$). These constituents are dissolved in the water film at the leaf surface, and subsequently the reactants are released ($\text{SO}_4^{2-}$, $\text{NO}_3^{-}$) accompanied by base cations to the throughfall water. The throughfall water is distributed in specific patterns by the leaves as well as by the stem and crown structure. This leaching from canopy can change element fluxes with throughfall considerably, especially nitrogen and proton fluxes [43,44]. In particular, stem flow can evoke acidic hot spots in the soil around the trees [25].

Another source of heterogeneity is the soil structure with different reaction compartments. In fast-draining pores, water can pass through the soil without major chemical reactions with the soil surface. In contrast, in slow-draining pores the water can equilibrate with the soil surface and the pore water. Thus, the chemical composition of the draining water will change in accordance with a decreasing pore diameter. The travel time of the water depends on the rainfall intensity, soil water status (wet, dry), hydraulic gradient, and local soil structure (relative proportions of coarse and fine pores). The extent of element loading from the soil into the passing water depends on the actual exchange capacity of the local soil surface, chemical reactions (such as mineralization), a lack or surplus of the transported water, and root uptake.

Figure 1 shows the coefficients of variance for pH, $\text{SO}_4^{2-}$, and $\text{NO}_3^{-}$ for four compartments: precipitation, throughfall, mineral soil, and runoff. The variance in precipitation is lowest of all compartments. A great increase in heterogeneity for all elements except $\text{Cl}^{-}$ can be observed in throughfall when the water has passed the crown compartment. The maximum heterogeneity is reached in soil solution at 20-cm depth. With increasing soil depth, this influence diminishes. In runoff, heterogeneity reaches the level of variance in the precipitation.

For $\text{Cl}^{-}$ the findings are different. This is because $\text{Cl}^{-}$ is a more or less inert element with respect to the soil. Therefore, the heterogeneity does not increase in soil solution. Nevertheless, the heterogeneity increases drastically in runoff as an effect of thawing salt infiltrating from a nearby country road.
Figure 1 Coefficient of variation (CV%) in precipitation (P), throughfall (TF), soil solution at different depths (20, 35, and 90 cm), and runoff (RO) for pH, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-}. The coefficient of variation has been calculated separately for the various sampling dates; only averages of these values are given. The data correspond to samples obtained from 1993 to 1999.
Therefore, to minimize sampling efforts for the investigation of mass balance, it would be best to investigate the fluxes in precipitation and runoff. However, with precipitation, only wet deposition is recorded. Other methods for recording dry deposition, such as surrogate surfaces or concentration gradient methods (eddy correlation), are representative only for larger scales in space and time or require uniform vegetation and adequate fetch [45]. However, for all methods it is true that the determination of total deposition from throughfall yields an underestimate of the actual deposition because the intake at the crown by needles and leaves is neglected [46].

At the runoff of a whole catchment, the heterogeneity will decrease with an increase in the portion of deep seepage water compared with the surface water (Fig. 2). On the other hand, runoff is often an unreliable estimate of the output flux with respect to unknown sinks or sources of water in the catchment (e.g., seepage in catchments that are not leakproof) and elements (e.g., fens). In addition, statements are possible only for the entire catchment, not for individual stands. Therefore, the only way to obtain representative results in such heterogeneous systems is to work with appropriate sampling sizes.

Ågren and Bosatta [47] suggested evaluating nitrogen saturation of terrestrial ecosystems for mass balances. In Fig. 3 the input–output mass balances for

**FIGURE 2** Heterogeneity of input and output fluxes in the catchment.
nitrogen are presented. Spatial heterogeneity of the 20 plots and temporal heterogeneity over the 7 years are obvious (Fig. 3, top). The balances are positive or negative over the years. It is obvious that results that consider only one or a few plots, e.g., when a restricted sampling size is taken into account, could be misleading.

The 95% confidence intervals (Fig. 3, bottom) often include zero. For this reason, evaluation of 20 plots did not provide grounds for a decision on whether those balances are positive, negative, or zero.

**FIGURE 3** Annual input–output balances (throughfall-seepage at 90 cm depth) of nitrogen (\(\text{NO}_3-N + \text{NH}_4-N\)) for the Coulissenhieb site, 1993–1999. (Top) Annual balances for 20 plots at the site; (bottom) average and 95% confidence interval for the 20 plots.
In general, to assess the ecosystem state by using nitrogen balances is very expensive (huge sampling effort) or very unreliable because of the limited sampling size. Because of these methodological deficiencies, logging all relevant nitrogen fluxes is an obvious choice.

2.4.2 Spatial Heterogeneity and Scale Dependences

A way to minimize sampling size is to detect spatial dependences and to develop a stratified sampling design based on these dependences. Figures 4 and 5 show the heterogeneity in pH, NO$_3^-$, and SO$_4^{2-}$ on the microscale (centimeters) and mesoscale (plots). No spatial correlation was found for pH with SO$_4^{2-}$ or NO$_3^-$. 

**Figure 4** Spatial distribution of the pH, SO$_4^{2-}$ and NO$_3^-$ values as measured by microlysimeters on the microscale. Interpolation was done by inverse distance weighing.
Scale-dependent variance of soil solution data is given in Table 1. Because spatial variability tends to decrease with depth [38], the intention was to obtain comparable depths. Mean values of the anion concentration at different scales differ by a factor of 2 to 3. Spatial heterogeneity of the ion concentration seems to be ion and scale specific. The coefficient of variance of NO$_3^-$ is largest in the micro

**FIGURE 5** Spatial distribution of the pH, SO$_4^{2-}$, and NO$_3^-$ values as measured by standard lysimeters on the macroscale. Interpolation was done by inverse distance weighing.
to macro range. The number of required samples in Table 1 indicates that for NO$_3^-$ up to 256 samples are required to determine the concentration with an accuracy of ±10%. The coefficient of variation (CV) of pH has a maximum at the microscale, and the CV of Cl$^-$ has a minimum at the macroscale. For SO$_4^{2-}$, there is a clear trend from maximum at the microscale to minimum at the macroscale.

**Table 1** Characteristics of Soil Solution Sampled at Different Scales$^a$

<table>
<thead>
<tr>
<th>Scale and characteristics</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>CV (%)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(microcups), n = 55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3.3</td>
<td>5.0</td>
<td>4.0</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>4.9</td>
<td>41.2</td>
<td>24.0</td>
<td>19.0</td>
<td>17</td>
</tr>
<tr>
<td>Cl</td>
<td>2.9</td>
<td>17.6</td>
<td>5.8</td>
<td>51.0</td>
<td>30</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>0.0</td>
<td>20.4</td>
<td>3.3</td>
<td>129.0</td>
<td>108</td>
</tr>
<tr>
<td>Mesoscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(four subsites), n = 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3.3</td>
<td>4.2</td>
<td>3.7</td>
<td>7.0</td>
<td>1</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>3.8</td>
<td>33.8</td>
<td>16.4</td>
<td>33.0</td>
<td>36</td>
</tr>
<tr>
<td>Cl</td>
<td>0.9</td>
<td>8.6</td>
<td>2.3</td>
<td>40.0</td>
<td>8</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>1.5</td>
<td>51.3</td>
<td>18.9</td>
<td>83.0</td>
<td>256</td>
</tr>
<tr>
<td>Mesoscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(25 m × 25 m grid), n = 59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3.4</td>
<td>4.4</td>
<td>3.8</td>
<td>7.0</td>
<td>1</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>7.4</td>
<td>36.0</td>
<td>15.5</td>
<td>36.0</td>
<td>40</td>
</tr>
<tr>
<td>Cl</td>
<td>1.6</td>
<td>16.1</td>
<td>5.3</td>
<td>50.0</td>
<td>26</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>0.0</td>
<td>40.1</td>
<td>10.5</td>
<td>77.0</td>
<td>123</td>
</tr>
<tr>
<td>Macroscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(different stands), n = 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>3.3</td>
<td>5.1</td>
<td>4.3</td>
<td>5.0</td>
<td>1</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>2.1</td>
<td>72.0</td>
<td>30.9</td>
<td>56.0</td>
<td>190</td>
</tr>
<tr>
<td>Cl</td>
<td>0.9</td>
<td>8.6</td>
<td>2.6</td>
<td>26.0</td>
<td>4</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>0.0</td>
<td>51.3</td>
<td>4.5</td>
<td>100.0</td>
<td>89</td>
</tr>
</tbody>
</table>

$^a$ Micro suction cups were positioned 12 to 28 cm deep, standard suction cups 20 cm deep (4 × 5 suction cups), 35 cm (25 m × 25 m grid) and 50 cm deep at the watershed scale. n = number of samples per date, N = required sampling size.

Mean and coefficient of variance have been calculated for various sampling dates separately, and median values were presented.
Analysis of correlation length was performed for soil solution samples by semivariograms. For microsuction cups, which covered a field of 8.14 cm$^2$, the correlation length is beyond the scale of the measurements. For the 25 m $\times$ 25 m grid, the correlation length is apparently less than the minimum sampling distance for all ions under study.

At the spatial scale for a whole state (Lower Saxony, Fig. 6), the heterogeneity of pH follows spacious geological formations: the Pleistocene sands in the north are associated with low pH, whereas in the south in the Lower Saxony mountainous region more base-rich rock formations, partially with lime, are associated with higher pH.

2.4.3 Temporal Heterogeneity of Soil Solution

From Fig. 7 (left side), the large temporal heterogeneity of SO$_4^{2-}$ concentrations in soil solution is obvious, especially in throughfall during the winter months due to the combustion of heating oil. This dynamics can also be seen in runoff but not in soil solution.

In general, a trend of diminishing SO$_4^{2-}$ concentrations in throughfall is clear. The concentrations in discharge and runoff follow the input trend. With the concentration decrease, the standard deviation decreases (Fig. 7, right side); i.e., the absolute variability decreases with decreasing concentrations. On the other

![Figure 6](image-url)
hand, the variation coefficient (i.e., the relative variability related to the average concentrations) remains unchanged (not shown).

2.4.4 Heterogeneity and Model Application

Results for \( \text{SO}_4^{2-} \) extracted from soil samples are listed in Table 2. The mean values decrease with scale by a factor of 3.5, whereas standard deviation increases by
a factor of 2, resulting in an increase in the coefficient of variation by approximately seven-fold.

In Table 3, model results are given for the range of measured isotherm parameters. Variation of isotherm parameters does not increase substantially with scale. As the SO$_4^{2-}$ concentration in the soil solution is near the maximum adsorption capacity of the soils, the effect of different isotherm parameters increases with decreasing SO$_4^{2-}$ deposition. Thus, differences in predicted SO$_4^{2-}$ concentration in the soil solution are most pronounced at approximately the year 2005. Fur-

### Table 2  H$_2$O-Extractable SO$_4^{2-}$ (μmol g$^{-1}$) in B Horizons at Different Scales

<table>
<thead>
<tr>
<th>Scale and horizon$^a$</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>CV (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_{hs}$</td>
<td>3.31</td>
<td>5.07</td>
<td>3.94</td>
<td>12.1</td>
</tr>
<tr>
<td>B$_s$</td>
<td>3.34</td>
<td>5.14</td>
<td>4.13</td>
<td>12.8</td>
</tr>
<tr>
<td>B$_v$</td>
<td>3.75</td>
<td>4.93</td>
<td>4.16</td>
<td>8.9</td>
</tr>
<tr>
<td>Total</td>
<td>3.31</td>
<td>5.14</td>
<td>4.09</td>
<td>11.2</td>
</tr>
<tr>
<td>Mesoscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_{sh}$</td>
<td>0.48</td>
<td>2.98</td>
<td>1.49</td>
<td>56.4</td>
</tr>
<tr>
<td>B$_s$</td>
<td>1.07</td>
<td>2.86</td>
<td>1.84</td>
<td>30.4</td>
</tr>
<tr>
<td>B$_v$</td>
<td>0.68</td>
<td>3.93</td>
<td>1.72</td>
<td>48.3</td>
</tr>
<tr>
<td>Total</td>
<td>0.48</td>
<td>3.93</td>
<td>1.63</td>
<td>49.7</td>
</tr>
<tr>
<td>Macroscale</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B$_{sh}$</td>
<td>0.14</td>
<td>0.78</td>
<td>0.47</td>
<td>48.9</td>
</tr>
<tr>
<td>B$_s$</td>
<td>0.20</td>
<td>2.98</td>
<td>1.42</td>
<td>60.6</td>
</tr>
<tr>
<td>B$_v$</td>
<td>0.13</td>
<td>2.75</td>
<td>1.22</td>
<td>74.6</td>
</tr>
<tr>
<td>Total</td>
<td>0.13</td>
<td>4.61</td>
<td>1.19</td>
<td>78.2</td>
</tr>
</tbody>
</table>

$^a$ B$_{hs}$ and B$_{sh}$ are B horizons influenced by sesquioxides and humic substances, B$_s$ is a B horizon influenced only by sesquioxides, and B$_v$ is a weathered B horizon.

$^b$ CV, coefficient of variation.

### Table 3  Simulation of the Sulfate Concentration with the MAGIC Model$^a$

<table>
<thead>
<tr>
<th></th>
<th>$b$ (mmol$_c$ kg$^{-1}$)</th>
<th>$C_{b/2}$ (mmol$_c$ m$^{-1}$)</th>
<th>SO$_4$ 1992 (mmol$_c$ m$^{-1}$)</th>
<th>SO$_4$ 2005 (mmol$_c$ m$^{-1}$)</th>
<th>SO$_4$ 2044 (mmol$_c$ m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>12.6</td>
<td>738.8</td>
<td>624.3</td>
<td>368.1</td>
<td>175.4</td>
</tr>
<tr>
<td>Upper</td>
<td>8.2</td>
<td>122.1</td>
<td>567.3</td>
<td>303.7</td>
<td>169.8</td>
</tr>
<tr>
<td>Mean</td>
<td>4.6</td>
<td>149.3</td>
<td>552.5</td>
<td>273.1</td>
<td>161.9</td>
</tr>
<tr>
<td>Lower</td>
<td>2.8</td>
<td>1796.0</td>
<td>544.7</td>
<td>227.5</td>
<td>159.1</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.6</td>
<td>54.2</td>
<td>533.1</td>
<td>211.5</td>
<td>159.4</td>
</tr>
</tbody>
</table>

$^a$ $b$ = sorption maximum (μmol g$^{-1}$), $1/k$ = half-maximum saturation point (mmol L$^{-1}$), which is equal to the SO$_4^{2-}$ concentration at $1/2$ $b$. SO$_4$ 1992, SO$_4$ 2005, and SO$_4$ 2044 are the simulated SO$_4^{2-}$ amounts per meter of soil for the years 1992, 2005, and 2044, respectively.
ther decreasing $SO_4^{2-}$ deposition decreases the influence of the shape of the isotherm curves, thus reducing spatial variation again.

2.4.5 Soil Chemistry and Timber Increment

The yield tables from Schober [48] allow comparison of the measured tree growth with a reference curve derived from long-term observations. In Fig. 8 the increment of the Solling site is compared with the yield table values. The increment developed from yield class III in 1965 to yield class I in 2000 (Fig. 8, bottom) in spite of the decreasing Ca/Al and Mg/Al ratios (Fig. 8, top).

![Figure 8](image_url)

**Figure 8** (Top) Time course of Ca/Al and Mg/Al ratios, with trend lines. (Bottom) Development of timber increment at the Solling site (·). For comparison, the yield table values for the site class I from yield table (upper line), site class II (middle line), and site class III are presented.
3 IMPLICATIONS

Two main aspects should be considered when investigating soil acidity. First is the soil–plant interaction aspect. Because of nutrient depletion and release of substances that are toxic to roots, a yield decrease is expected. On the other hand, an environmental aspect is the concern about the impairment of the sustainable yield potential of the soils and the release of detrimental substances from the soil to the environment.

Heterogeneity in soil solution for most elements is much higher than in throughfall or runoff. This has implications for soil–plant interactions. As in Figs. 5 and 6, the spatial pattern of soil fertility can be assumed for all soils. Dealing with this is different for different land uses. When growing an arable crop, the actual soil state can be deduced from the yield after harvesting. Deteriorated soil conditions will be indicated by a lower yield or changes in the plant content of various substances. Lowering yield can be alleviated by fertilizing and liming according to the yield pattern. The heterogeneity of the soil conditions and the different fertilizer demand can be manipulated through precision farming.

In forestry, the situation is more difficult. Fertilizer is hardly applied to forest soils for economic reasons. Because of the long-term harvesting periods in forestry, it is impossible to infer the actual soil state from the harvest. However, permanent increment measurements can fill the gap but are expensive and practicable only for a few trees.

As shown in Fig. 8, the spruce increment does not seem to reflect the deteriorated soil state as indicated by the Ca/Al or Mg/Al indicators. On the contrary, the spruce goes above the increment as defined by the conventional yield tables. Also, the element contents in the needles do not reflect the actual soil state [49].

One hypothetical explanation for this phenomenon is that high nitrogen inputs are responsible for the unexpected increment of the last decades. This was unexpected because the soil state indicated that sufficient nutrients, especially Mg could not be taken up by the roots. A suggestion was offered that Mg and other nutrients can be translocated from older needles into growing tips [50, 51]. However, on a long-term basis this would lead to a shortage of Mg and other nutrients because of losses. Therefore, the long-lasting increment can be explained only partly by this hypothesis.

Part of this phenomenon can be explained by soil heterogeneity. The Ca/Al and Mg/Al indicator has been deduced from hydroponics experiments, i.e., an absolute homogeneous environment for the root. Under field conditions, the Ca/Al values measured in lysimeters may not reflect the actual soil state as seen by the tree roots. First, it does not reflect the fact that roots can grow to the soil organic horizon to explore the nutrients from the yield.

The soil water from fast-draining pores is overrepresented in the collected lysimeter water. Lysimeters collect relatively more water from the fast-draining
pores because of the limited suction (200–300 mbar) at which the lysimeters were maintained. Further, they collect unspecific water, but not in the microcompartments from which the roots take up water and nutrients. The fast-draining pores seem to be hardly used by the tree roots because the pores are quickly filled with the infiltrating water but also as quickly emptied because the water is not retained against gravity. Therefore, this pore class is less suitable for sustainable water supply for roots. Tree roots have sufficient dynamics to avoid such detrimental zones and to search actively for more suitable microcompartments. Nutrient- and base-rich water is more likely to be found in smaller pores because the time the water can come in equilibrium with the cations from the mineral surface is longer.

Thus, the soil situation might look worse when analyzing the lysimeter water compared with the actual situation experienced by the roots. In this sense, soil heterogeneity can contribute to the survival of trees in otherwise unfavorable environmental conditions. Therefore, indicators such as Ca/Al should not be directly transferred from hydroponics experiments. To characterize the effective soil state under field conditions, spatial and temporal distributions seem to be more suitable.

Maps of the spatial distribution of the element concentrations, especially those measured in microlysimeters, might yield further insights into whether the soil has enough microcompartments with suitable living conditions for roots. Micro scale heterogeneity of soil solution should especially be considered when investigating root uptake because roots are very dynamic in avoiding detrimental soil zones and finding nutrients. An acidification indicator averaging different soil horizons could be misleading. This is confirmed by studies showing that soil acidification will decrease the fine root mass of trees and shift the rooting zone to upper, more nutrient-rich soil layers [52,53].

The reaction of the trees to increasing soil acidity cannot be understood without analyzing the temporal and spatial variability of acid stress [54]. Studies of resource distribution in forested ecosystems need to consider not only the average levels but also the variance, frequency, and spatial distributions of these resources [55]. In middle Europe, the concentrations of $\text{SO}_4^{2-}$ in precipitation and throughfall are decreasing. In parallel, the variability is decreasing, as can be seen from Fig. 7, with the consequence that acid stress by sulfate peaks is reduced.

The time dependence of spatial variability is also illustrated by the application of the MAGIC model. The variation of isotherm parameters influences the variability of the computed $\text{SO}_4^{2-}$ concentration in soil solution. Without knowledge and use of isotherm variability, no statements about modeling insecurities are possible. Model results without an estimate of the error range of the results provide limited evidence.

The correctness of the critical loads approach for acidic deposition into forest soils is questionable [6]. The problem demands a more dynamic approach that takes into account the temporal and spatial variability of terrestrial ecosystems. According to Ulrich and Summer [56], under high acid deposition and on less
buffered soils, short-term strain (temporal heterogeneity) will occur more often and so destabilize the ecosystem.

Due to the long-distance transports of the gaseous components, critical loads are spatially applicable only. One should commit critical levels means to consider the weakest link. However, at the site of the strong heterogeneity, one is not likely to find any region that will not have at least a few very sensitive spots. As a consequence, the acidic emissions have to be further reduced to accommodate the sensitive spots.

Important for environmental aspects are balances and fluxes of the matter in ecosystems because they indicate nutrient losses for the system or the release of detrimental substances to adjacent ecosystems.

It has been demonstrated that the degree of heterogeneity at a given observational scale is strongly dependent on the chemical species considered; e.g., NO$_3^-$ in soil solution seems to be especially costly to measure adequately with a prescribed accuracy. Because of the heterogeneity, a large number of replications are necessary [18]. The fluxes of matter can, with reasonable efforts, be calculated only with limited precision. Spatial heterogeneity at all scales has to be taken into account. To determine the average with an appropriate accuracy sampling, up to 256 replicates are necessary for soil water, as found in this study. Conclusions from investigation of the matter flux have to consider the error ranges. However, due to errors, the sharpness of the statements decreases and recommendations, e.g., on fertilizing, become imprecise. The utilization of input–output balances to characterize ecosystem states of N saturation is especially unreliable and limits practical importance. Small-scale spatial and temporal variation occurs. The state of N saturation can vary spatially at small scales, as shown in Fig. 3. These dynamics in soil have been investigated as fingering [57]. The temporal dynamics of the state of N saturation have the consequence that balances at one plot differ from year to year, which makes statements on N saturation unreliable. This complicates concrete measures (opening up, tillage) to manipulate the N pool in the ecosystem.

Variogram analysis gave evidence that correlation length is between the resolution of the micro- and the normal-sized soil suction cups (2 cm and 2 m, respectively). This is in accordance with, e.g., Simmonds and Northcliff [58], who determined a correlation length of Br$^-$ and Cl$^-$ transport in a sandy loam of approximately 35 cm. The dependence of NO$_3^-$ concentration in soil solution and catchment runoff on a variety of different parameters (Table 2) indicates that different deterministic length scales overlap. For the investigated sites this would indicate that no additional heterogeneity can be found on the macroscale.

4 CONCLUSIONS

Measurement concepts should consider intensive spatial and temporal investigations of relatively small plots. They will be representative of the surroundings. In-
tensive measurement plots seem more appropriate for further understanding of soil reactions and the integration of heterogeneity in the evaluation. Spacious assessment based on the almost uncertain estimation of local soil properties by means of geographic information systems is inadequate because the validity and implications for the ecosystem of such results cannot be estimated at present.

REFERENCES


Measurements of H⁺ Fluxes and Concentrations in the Rhizosphere

Benoît Jaillard, Claude Plassard, and Philippe Hinsinger
UMR Soil and Environment, INRA, Montpellier, France

1 INTRODUCTION

Soil pH is probably the most important chemical soil parameter [1]. It reflects the overall chemical status of the soil and influences a whole range of chemical and biological processes occurring in the soil. Because of its implications in most chemical reactions in the soil, knowing the actual value of soil pH and monitoring its changes is critical for understanding the physicochemical functioning of the soil.

During plant growth, roots exchange a number of substances with their environment, thus ultimately modifying the physicochemical conditions of the soil solution, its pH in particular [2,3]. These pH changes result mainly from two processes. First, roots and rhizosphere microorganisms rely on root exudates to produce CO₂ through respiration. The buildup of CO₂ partial pressure thereby occurring in the rhizosphere can contribute to some acidification [4]. In acid soils this is of restricted significance, as at low pH carbonic acid remains mostly undissociated in the soil solution, its first pK being 6.36 [5]. The second and major origin of pH changes in the rhizosphere is related to the release of H⁺ or OH⁻ to counterbalance a net excess of cations or anions, respectively, entering the roots [6,7].
For further details on this cation–anion balance, the readers are referred to Chapter 3 in this book. These processes can be affected by environmental stresses; Fe deficiency [8] and P deficiency, the latter being more relevant for acid soil conditions, can both enhance H$^+$ release by plant roots [9,10]. Aluminum toxicity is another common stress that plants can experience in acid soils and which can influence these processes. Indeed, as reported for corn, for instance, Al toxicity results in enhanced H$^+$ release via a reduction of nitrate uptake and little concomitant effect on cation uptake, especially so in Al-sensitive genotypes [11–13]. For an extensive review of the diverse origins of root-induced pH changes that can occur in the rhizosphere, see Nye [6,14], Haynes [7], Marschner [2], or Hinsinger [3].

The actions exerted by roots are localized and confined to the rhizosphere, i.e., the volume of soil that is directly influenced by plant roots [15]. The resulting changes in pH can be considerable, reaching one to two pH units [2,3,16]. Such changes are of major ecological significance because of their possible effects on the physiological activity of the roots and rhizosphere microorganisms and because of their influence on the bioavailability of mineral nutrients and potentially toxic substances in soil. It is therefore of prime importance to take account of H$^+$ fluxes occurring in the rhizosphere and to have access to the actual values of pH that plant roots can experience. The aim of this chapter is to review the techniques developed for this purpose. As the rhizosphere is a restricted volume of soil around roots that is rather difficult to access for in situ and to sample for ex situ measurements, a range of methods have been designed to overcome this major difficulty. The advantages and major limitations of each of these approaches will be discussed. The first part will focus on the methods used for measuring H$^+$ ions that are released or taken up by roots growing in solution culture, without any solid phase. The second part will review the methods used for measuring the induced pH changes in the rhizosphere of soil-grown plants. This chapter will show that, in spite of the considerable advances in the knowledge of the physiological functioning of roots in controlled, more or less artificial conditions, the various consequences in terms of pH changes in natural conditions, and more generally of physicochemical conditions in the rhizosphere, are still largely unknown. This is mainly due to the many methodological difficulties encountered in measuring soil parameters that are as crucial as pH at the scale relevant to the rhizosphere.

2 MEASUREMENTS OF FLUXES OF H$^+$ RELEASED BY ROOTS IN SOLUTION

2.1 Measurements by Titrimetry

When plants grow in solution, the net amounts of H$^+$ released by the whole root system can be measured by monitoring the changes in the solution pH as a function of incubation or culture duration. The given amount of H$^+$ ($\Delta[H^+]$) released
by roots is related to the pH change in the solution (ΔpH) according to the following relation:

$$\Delta [H^+] = -\beta \Delta pH$$  \hspace{1cm} (1)

where $\beta$ is the $H^+$ buffering capacity of the solution. Two methods are used: (1) the pH is not controlled during the period under study and samples of solutions are periodically back-titrated to the initial pH, making it possible to calculate the net $H^+$ fluxes corresponding to the variation of pH, or (2) the pH is maintained constant during the culture using a pH-stat device and the net $H^+$ fluxes are calculated from the amounts of base or acid added during the culture.

2.1.1 A Basic Method, the Back-Titration of Culture Solutions

The method of back-titration of solutions is simple to carry out and has therefore been used by many authors [17–21]. However, to get the actual fluxes of $H^+$ produced by root activity, the culture solution must have a constant and known, or very low and consequently negligible, buffering capacity. In the case of complete nutrient solutions, the buffering capacity results mainly from inorganic phosphate and carbonate. The concentration of carbonate in the bathing solution originates from respiration of roots or from the dissolution of gaseous $CO_2$ from the atmosphere. The main contribution of $CO_2$ to $H^+$ buffer capacity of the solution is due to the first dissociation of carbonic acid $H_2CO_3$ to $H^+$ and $HCO_3^-$; the pK of the reaction is 6.36 and the buffering capacity becomes important at pH greater than 6.0. Studies carried out on castor bean ($Ricinus communis$ L.) plants grown at pH 6.5 with $NO_3^-$ as the sole source of N demonstrated the importance of bicarbonate in the total amount of base (i.e., $OH^-$ and $HCO_3^-$) excreted by the plants during the growth period [17]. Indeed, back-titration of the culture solution to the initial pH of 6.5 led to underestimation by 50% or more of the actual amount of base released by the plants. The total amount of base excreted could be calculated only from data obtained by titration to pH 4.5, when almost all $HCO_3^-$ in the system was converted to $H_2CO_3$ and then evaporated to $CO_2$. Indeed, comparison of the $HCO_3^-$ concentration in the culture medium after plant growth with the $HCO_3^-$ concentration predicted from atmospheric $CO_2$ showed that aqueous $H_2CO_3$ was not in equilibrium with atmospheric $CO_2$; the solution was supersaturated to a considerable degree, suggesting a high concentration due to the respiratory activity of the roots together with a slow rate of evaporation of $CO_2$. On the contrary, with castor bean grown at pH 6.5 in $NH_4^+$-nutrient solution, the effects of phosphate uptake and ionic strength changes on base titrimetry of excreted $H^+$ were scarcely significant, with underestimation of $H^+$ release not greater than 3% [18]. In this case, $NH_4^+$ uptake resulted in an acidification of the solution to below pH 6.0. Under such conditions $H_2CO_3$ remained largely undissociated and hence root respiration did not contribute to acidification of the solution.
The reliability of the back-titration method strongly depends on the initial pH, the buffering capacity of the solution, and especially the concentration of bicarbonate, which may vary strongly during the measurement. In addition, the change in pH occurring during uptake or growth can modify the uptake rates of the ions under study. This problem was solved by using experimental devices that make it possible to automatically maintain the pH at its initial value, the so-called pH-stat devices.

2.1.2 The More Advanced pH-stat System

This method is based on continuous monitoring of the H+/H₄⁺ or ion under study with a pH electrode or an ion-specific electrode. The electrode is connected to dosing pumps that automatically deliver known volumes of solution when the actual H⁺ or ion concentration deviates from its initial fixed value. In the case of H⁺, such a system is called a pH-stat system and requires one or, if possible, two dosing pumps for adding acid or base to the culture solution according to the direction of pH change. The system can be computer controlled and maintain constant K⁺ and NO₃⁻ [22], H⁺ and NO₃⁻ [23], or only H⁺ concentrations [24,25]. The net fluxes are then calculated from the successive additions of the solutions containing the ion considered. With this experimental system, it was confirmed that NO₃⁻ uptake by plant resulted in a net alkalinization of the solution [23,25], whereas NH₄⁺ uptake resulted in a net acidification [25] (Fig. 1).

The main advantage of the pH-stat system is the possibility of monitoring over time the net fluxes of H⁺ released by the whole root system and their kinetics as a function of any factor (such as the source of mineral N) without any significant changes in pH, which could in turn modify the uptake rate of other ions. However, the method does not make it possible to observe heterogeneities in root functioning. To address this question, it is necessary to use other local methods such as micropotentiometry.

2.2 Local Measurements by Micropotentiometry

2.2.1 Liquid Membrane Ion-Selective Microelectrode

Local net fluxes of H⁺ can be determined with ion-selective microelectrodes. The main type of electrode used for ion flux measurements in solution is the liquid membrane microelectrode. Lucas and Kochian [26] initiated this technique to estimate the net flux of H⁺ from roots by measuring the gradient of electrochemical potential of H⁺ in the solution close to the root surface. The technique of microelectrode ion flux estimation has been used subsequently by many researchers to estimate H⁺ fluxes at the surface of roots [27–38].

The development of ion-selective microelectrodes was pioneered by Walker [39] and Thomas [40] in the 1970s. A microelectrode consists of an ion-selective liquid membrane enclosed in a fine glass capillary. The liquid membrane must be
hydrophobic to separate the internal reference phase from the solution to be measured. It is therefore necessary to make the inner side of the glass capillary hydrophobic. This is carried out by silanization, the quality of which determines the electrode performance \([41,42]\). The electrode selectivity depends upon the nature of the liquid membrane, generally called a cocktail. Today, many different ready-for-use cocktails are commercially available and make it possible to design microelectrodes that are selective for several ions: \(\text{H}^+ / \text{H}_2\text{O}^+\), \(\text{Na}^+ / \text{H}_2\text{O}^+\), \(\text{K}^+ / \text{H}_2\text{O}^+\), or \(\text{Ca}^{2+} / \text{H}_2\text{O}^+\). The activities of other ions such as \(\text{NO}_3^-\) and \(\text{NH}_4^+\) can be measured with mixtures that

\[\text{FIGURE 1} \] Stoichiometry of \(\text{H}^+ / \text{NH}_4^+\) (a) and \(\text{H}^+ / \text{NO}_3^-\) (b) exchanges by corn. The data were measured by titrimetry using a pH-stat system. (Redrawn from Ref. 25. Copyright 1997, Blackwell Science Ltd, UK.)
must be prepared by the operator. After silanization of the glass capillary, its tip is filled with less than 1 μL of the selective membrane before back-filling the capillary with a saline solution containing the ion to be measured. Intact electrodes have a tip diameter smaller than 1 μm and a resistance in the order of $10^{10}$ Ω. Breaking the tip decreases its resistance and the response time of the electrode; a tip 5 μm in diameter gives good performance. Because of this high resistance, an electrometer with very high input resistance (at least $10^{14}$ Ω) is required [32] and the whole measuring device must be insulated by and grounded to a Faraday cage.

2.2.2 Principle of Ion Flux Determination

Root geometry may be approximated by a cylinder with ion flux presumably occurring in the radial direction only [43]. This hypothesis leads to expressing ion flux by a simple relation between concentration and distance to the geometrical axis according to the equation

$$J = \frac{2\pi D (C_2 - C_1)}{\ln(R_2/R_1)}$$

where $J$ is the ion net flux per unit length of root, $D$ is the self-diffusion coefficient of the studied ion, and $C_1$ and $C_2$ are its concentration at the two radial distances $R_1$ and $R_2$ from the geometrical axis of the root [27,29,30]. Experimentally, the hypothesis of a cylindrical geometry for roots can be checked by measuring ion concentrations at various distances from the root axis (Fig. 2). The concentrations in solution are calculated according to Nernst’s law:

$$C = \exp\left(\frac{\mu - \mu_0}{RT}\right)$$

where $\mu$ and $\mu_0$ are the sample and standard electrochemical potentials of the studied ion, $R$ the constant of perfect gases, and $T$ the absolute temperature. Microelectrodes are calibrated in standard pH solutions in order to calculate the Nernstian slope, which generally varies between 56 and 58 mV per logarithmic unit of concentration.

The main error in the flux calculation is due to the error in positioning the microelectrodes relative to the root axis, especially for fine roots [43]. Indeed, one of the trickiest steps of this method is to measure accurately the root diameter and the radial distance of the microelectrode from the root surface. This must be carried out under microscope magnification using a calibrated eyepiece reticle [43,44] or a computer-controlled motor-driven translation stage [38]. The positioning of microelectrodes in the unstirred layer can be achieved by moving the microelectrode itself by using a motor-driven micromanipulator that supports the microelectrode holder [27,30,32,43,44] or the root under study. In the latter case, the cuvette containing the root is placed on top of a computer-controlled motor-driven translation stage allowing vertical movements with micrometric precision [38].
As previously pointed out, the observed H\(^+\)/H\(_{11001}\) fluxes can be different from the actual ones due to the buffering capacity of the solution. This problem was addressed from a theoretical point of view [45]. Regarding the utilization of buffered solution, it is possible to calculate the protonated buffer flux from the measured H\(^+\)/H\(_{11001}\) flux in solution. However, unbuffered solutions always have the buffering effects of water itself and more so of carbonates due to CO\(_2\) dissolved from the atmosphere. The calculations demonstrated that in such solutions at pH 6.0 the flux carried by water and carbonates is about 1% of the measured H\(^+\)/H\(_{11001}\) flux. However, as previously mentioned [18], respiratory CO\(_2\) produced by the root itself can have an important buffering effect, especially at pH higher than 6.0. Until now, this respiratory effect has never been taken into account, but this problem undoubtedly deserves further attention.

2.2.3 Coupling the Measurement of H\(^+\) Fluxes and Ion Uptake Along the Roots

The microelectrode technique allows direct, noninvasive measurements of ion fluxes between tissues and the surrounding solution. These measurements are instantaneous and have a high spatial resolution due to the small size of the microelectrode tip, making it possible to identify differences in root activity over short distances (Fig. 3). In addition, ion fluxes can be measured at low external ion concentrations, generally in the micromolar range. H\(^+\) and K\(^+\) microelectrodes were

**FIGURE 2** Profile of K\(^+\) (■), NO\(_3^-\) (□), and H\(^+\) (+) activities as a function of \(\ln(R_2/R_1)\), where \(R_1\) is the radius of the root and \(R_2\) the distance to the root axis, for a primary root of corn. The data were measured using ion-selective glass microelectrodes. (Redrawn from Ref. 38. Copyright 1999, Kluwer Academic Publishers, Netherlands; and from Plassard, unpublished).
used to study the coupling between both ions, especially when external K\(^+\) was supplied at low concentration (in the micromolar range). The hypothesis was that K\(^+\) uptake is coupled, either directly or electrophoretically, to H\(^+\) efflux. However, experimental data [27,28] from simultaneous measurements of fluxes did not support either form of coupling. In addition, the measurements of membrane potential carried out simultaneously during K\(^+\) uptake suggested that K\(^+\) influx occurred via a highly electrogenic process [27]. It was hypothesized that, at low K\(^+\) concentration, K\(^+\) uptake might be mediated by a K\(^+\)/H\(^+\) cotransport system instead of an antiport one. This hypothesis was finally confirmed using a molecular approach [46].

Another coupling extensively studied with ion-selective microelectrodes was the coupling between H\(^+\) and NO\(_3\). Although it was established that nitrate...
uptake leads to alkalinization of the nutrient solution, it was not clear whether 
NO$_3$ uptake occurred via an H$^+$/NO$_3$ symport or an OH$^-$/NO$_3$ antiport. This 
question was especially studied with corn roots. The first results showed that ni-
trate uptake resulted in a strong membrane hyperpolarization and was not associ-
ated with an increase in the inorganic carbon efflux, strongly suggesting the oper-
ation of an OH$^-$/NO$_3$ antiport [47]. Further study of the effect of NO$_3$ uptake on 
membrane depolarization revealed that a transient depolarization was occurring 
before the hyperpolarization [48]. It was concluded that the depolarization was 
due to the operation of an H$^+$/NO$_3$ symport and that the subsequent hyperpolar-
ization resulted from the stimulation of the plasma membrane, occurring secon-
darily from the operation of the H$^+$/NO$_3$ symport. Finally, the authors concluded 
that their data provided evidence for the operation of an H$^+$/NO$_3$ symport with a 
stoichiometry that differed from the unity [30]. A comparison of H$^+$ fluxes deter-
mimed along corn roots using selective microelectrodes after growth with NH$_4$ or 
NO$_3$ confirmed the low values of H$^+$ fluxes in the presence of NO$_3$ in the solu-
tion [38,49].

In addition, ion-selective microelectrodes made it possible to investigate the 
eye consequences of different stresses applied to roots, such as wounding 
[31,50], osmotic or temperature stresses [34,35], and Al toxicity [51,52]. For in-
stance, a concentration of 10 $\mu$M Al$^{3+}$ inhibited both the net H$^+$ current and root 
growth of an Al-sensitive wheat cultivar within only a few hours, whereas no 
change in either current magnitude or root growth was observed with an Al-toler-
ant wheat cultivar [51]. Measurements with ion-selective microelectrodes demon-
strated that H$^+$ influx was responsible for most of the current at the root tip, with 
smaller contributions from Ca$^{2+}$ and Cl$^-$ fluxes.

### 2.2.4 Limits and Advantages of the Microelectrode Ion 
Flux Estimation

The microelectrode technique enables noninvasive measurements of ion fluxes in 
space and time and appears to be a promising tool to study local variations in H$^+$ 
fluxes as a function of various factors. These can consist of physical or chemical 
treatments applied to the plant before or during the measurements, such as using 
nutrient solutions containing various ionic concentrations or composition. Al-
though this method has been used in herbaceous species, it should also be conve-
nient to determine H$^+$ fluxes along heterogeneous root systems, such as those of 
woody plants.

The method, however, has some limits. The major limitation is related to the 
possible errors in flux calculation as previously discussed. A second one is related 
to the variability of fluxes that have been observed in some cases. However, this 
problem can be minimized by using a flowing nutrient solution during the exper-
iment [38]. Another limitation is represented by the time required to carry out one 
scan, restricting the possibility of scanning a whole root system, contrary to other
methods, such as the agar-indicator method (see Sec. 2.3). Finally, the intensity of the fluxes can be too low to be measurable with microelectrodes. However, this can be solved by using a vibrating ion-selective microelectrode system that has better sensitivity than conventional microelectrodes [29].

2.3 Local Measurements by Colorimetry
2.3.1 A Simple Method to Monitor pH Changes Induced by Roots in Their Environment

The staining reactions of dye indicators have been used in chemistry, biology, and geology for a long time. They make it possible to follow the progress of chemical reactions and to identify the nature of specific components or the location of tissues or minerals. These methods are based upon the change in optical properties of molecules according to their chemical status or the formation or disappearance of colored substances. They are generally rapid and easy to use but qualitative rather than quantitative. In physiology and soil–root interaction studies, they have been used mainly for monitoring reduction and acid–base reactions or activity of compounds such as enzymes [53–56].

The use of dye indicators to reveal and locate the activity of H⁺ release by roots was proposed by Weisenseel, Dorn, and Jaffe in 1979 [57]. These authors were studying the steady electric currents around growing plant cells such as pollen tubes or root cells. These endogenous currents occurring around roots of higher plants had been known for many years and had raised many questions [58]. Using the vibrating probe technique, which is based on the measurement of the voltage difference between the two points of vibration probe positioning [59,60], Weisenseel et al. [57,61] showed that the electric currents entered at the level of the growing parts of pollen tubes, root apices, and root hairs and left out the other parts of cells or roots. Using bromocresol purple, a pH dye indicator, included in an agar sheet to visualize H⁺ dynamics around roots, these authors showed that the electric currents corresponded mainly to H⁺ fluxes around the root cells and root hairs. The pH around the apical and basal zones of roots and the basal zone of root hairs increased, showing inward H⁺ flux, whereas pH strongly decreased along the elongation zone of roots and at the tip of root hairs, showing outward H⁺ flux.

This work was important for several reasons. First, it confirmed that, with plants as with animals, the electric and electrogenic processes play a fundamental role in cell growth. Their location, direction, and intensity determine the growth of an isolated cell as well as the development of plant organs. Second, it established the relationship between endogenous electric currents and H⁺ fluxes. The electric currents that had been studied for many years in plants were mainly supported by fluxes of H⁺. With roots, the charge fluxes were induced by ion exchange activity between the root and its environment. Finally, these authors rein-
introduced an old but simple and effective method for monitoring these charge fluxes, to locate them, to determine their direction, and to estimate their intensity. Since then, this method has been adopted by many authors and has yielded important results on root growth and exchange activity.

2.3.2 Growth, Geotropism, and Electrogenic Activity of Roots

The following studies based on the preceding method had two main objectives. The first one, following the footsteps of Weisenseel et al. [57], was aimed at establishing the relationship between growth and electrogenic activity of roots. The ultimate objective was to verify the hypothesis of acid growth [62–64]. This theory was based upon the fact that cell wall elongation was favored under acidic conditions. Therefore, it hypothesized that plants developed specific adaptations to acidify cell walls where cells are growing. The electric currents being mainly supported by H⁺/H⁻ fluxes, it became easier and faster to measure directly these fluxes or their consequences in terms of pH change around the roots. Moreover, the color changes of a dye indicator made it possible to obtain, within a few minutes, an overall picture of the behavior of the whole root system.

Mulkey and Evans [65] studied the qualitative response of plants subjected to different stimuli in terms of direction of H⁺/H⁻ flux in different parts of plant roots embedded in an agar gel that contained a dye indicator [65,66]. Thereby, they showed that a growth inhibitor stopped the root elongation and the H⁺ flux simultaneously. Also, the geotropism appeared as differential growth of the upper and lower sides of the root, which induced the gravicurvature of the root. At the same time, the upper side of the root that grew faster released much more H⁺ than the lower side that grew more slowly [65]. These results were confirmed later by quantitative measurements with micropotentiometry [67].

Other authors have tried to quantify the color changes of a pH dye indicator. Pilet, Versel, and Mayor [68–70] focused their research on the topological and quantitative relationship between elongation and H⁺ flux along the roots. The variation of elongation rate along the roots was measured using beads glued on the root surface whose positions were determined at different time intervals. The rate of H⁺ release along the same roots was evaluated using these porous beads, which had been immersed in a solution containing the appropriate pH indicator. The color changes of the beads were then estimated visually by referring to a color standard scale that had been obtained independently in controlled conditions. This original and elegant work clearly demonstrated that the elongation rate of the root cells was closely related, in terms of location and intensity, with the H⁺ flux released by roots. With corn, the H⁺ efflux was maximal at about 3–4 mm from the root tip, where the cell elongation was also maximal [68]; the initial pH was 6.8, and the pH drop reached 1.8 pH units at the root surface. The intensity of the pH drop increased with root growth rate [69].
2.3.3 Environmental Conditions, Mineral Nutrition, and Charge Efflux from Roots

The second group of studies involving the agar-indicator method was aimed at evaluating the effect of environmental conditions on the mineral nutrition of plants and the charge flux consequently released by roots in their environment. The ultimate objectives were (1) from an ecological point of view, to improve our understanding of the adaptive responses of plants to different soil conditions, and (2) from a physiological point of view, to have a better understanding of the processes used by plants for modifying their immediate environment and, thereby, for mobilizing the mineral nutrients.

Marschner, Römheld, and coworkers have widely used and improved the method of pH dye indicators, and more generally several other methods of staining, for their ability to yield overall pictures of the behavior of the whole root system of plants in response to environmental conditions [55,56]. These authors have especially studied the diverse strategies that plants have developed for iron acquisition in soils. Iron is a poorly mobile element in most soils, especially when it occurs as FeIII (oxidized state). Plants have developed several mechanisms to increase FeIII solubility, transport, and uptake (e.g., reducing activity, release of H+/H11001, organic anions, and phytosiderophores by roots [71,72]). Previous results showed that root tips exerted specific chemical actions, among which H+/H11001 release has a strong effect on Fe mobility. The staining methods were well adapted to demonstrate, locate, and estimate the intensity of root actions. For this purpose, Römheld and Marschner have been using several indicators included in agar films: (1) a red-colored chelate of FeII for demonstrating Fe reducing activity, (2) a brown precipitate of MnO2 for showing Mn reducing activity, and (3) bromocresol purple for detecting H+/H11001 release by roots [73]. The results obtained with these three visual methods were very demonstrative. They showed that, in dicots, the iron deficiency enhanced the reduction of FeIII in the medium and the release of H+/H11001 by roots (Fig. 4). These processes were generally located around the root tips, where changes in cell structure were also reported [74].

The agar-dye indicator method also contributed to elucidating the cation–anion balance in plants and the direction of charge fluxes that were exchanged between roots and soils according to different environmental constraints: nitrogen nutrition [8,75,76], nature of ions [75], mineral nutrient deficiencies such as Fe or P [73,76,77], plant species [74,78], or symbiotic status of legumes [8]. Generally speaking, these studies underlined the ecological significance of (1) the direction and the intensity of charge flux released by roots and the induced pH changes in the rhizosphere, which significantly modify the root environment and the mobility of mineral nutrients, and (2) the location of H+ extrusion in certain zones of roots, thus concentrating H+ in small volumes of rhizosphere and increasing the efficiency of roots in mobilizing soil mineral nutrients.
2.3.4 Principle, Advantages, and Limitations of the Agar-Indicator Method

The agar-indicator method has been generally used as a qualitative method. Very few workers have tried to quantify this color-based information [68,70,71,79,80]. It is nonetheless a classical colorimetric method that can be easily used for quantitative purposes by using a spectrodensitometer [77,81]. Only three indicators have been selected and used because they do not have any harmful effect on the growth and exchange activity of roots: bromocresol green, bromocresol purple, and phenol red. It has, however, been reported that the phenol red reduced the growth of barley roots [57]. These three indicators are sulfonphthaleins acting as weak acids in water, with pK values of 4.7, 6.4, and 7.8, respectively [81].

FIGURE 4 Effect of Fe deficiency on H⁺ release by sunflower roots. Images with (a) and without (b) Fe supply were obtained using a pH dye indicator technique. The white zones indicate local acidification of the medium to pH 5.0 and lower. (From Ref. 8. Copyright 1984, American Society of Plant Physiologists, USA).
color change results from a shift in the equilibrium between only two forms, phenolic and quinonic. We can thus write
\[ \text{AH} \leftrightarrow \text{A}^- + \text{H}^+ \] (4)
with
\[ K = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]} \] (5)
or
\[ K = \frac{(1-x)}{x[H^+]} \] (6)
where \( K \) is the dissociation constant of the indicator, and \( x \) is the molar fraction of the indicator in acidic form, \( x = [\text{AH}]/([\text{A}^-] + [\text{AH}]) \). The optical density of the solution (\( D \)) is determined by the proportion of each form present at any given wavelength for a given concentration of indicator, as shown by the relation
\[ D = xD_A + (1-x)D_B \] (7)
where \( D_A \) and \( D_B \) are, respectively, the optical densities of the acidic and alkaline solution [82]. By combining Eqs. (6) and (7), we can write
\[ [\text{H}^+] = \frac{K(D - D_B)}{(D_A - D)} \] (8)
then
\[ \text{pH} = pK + \log \left( \frac{D - D_A}{D_B - D} \right) \] (9)
This relation leads to using acidic and alkaline standard agar sheets as calibrating references for \( D_A \) and \( D_B \). It is important that the thickness of the agar sheets is constant on the whole analyzed area (for applying the Beer–Lambert law). To facilitate the measurement, the pH of the agar sheet can be mapped directly using a scanning video camera connected to a computer for calculation and image analysis [82] (Fig. 5). The pH images can then be converted into images of total \( \text{H}^+ \) concentration in the medium, knowing its \( \text{H}^+ \) buffering capacity according to Eq. (1). The \( \text{H}^+ \) fluxes along roots are then calculated as the differences in total \( \text{H}^+ \) concentrations at different time intervals [13,38] (Fig. 5). Videodensitometry is in good agreement with other methods such as micropotentiometry [38].

The main advantages of the agar-indicator method are its simplicity and its ability to determine at once the response of the whole root system of a plant. It has
often been used for prospective studies or in addition to other methods that are more time consuming or more sensitive but local, such as micropotentiometry. The major limitation is the necessary transparency of the medium for valuable quantification. However, the agar-indicator method remains a convenient method to explore diverse plant species or genotypes or environmental conditions and surely the most didactic method to demonstrate the chemical actions that plant roots exert on their environment.

**FIGURE 5** pH map (a) and profile of $\text{H}^+$ efflux (b) along a primary root of corn grown at pH 4.6. The data were measured by videodensitometry of a pH dye indicator. (a) White zones indicate local acidification, dark zones local alkalinization. The gray level changes each 0.05 pH units. (Redrawn from Ref. 82. Copyright 1996, Kluwer Academic Publishers, Netherlands).
3 MEASUREMENTS OF H⁺ CONCENTRATIONS IN THE RHIZOSPHERE

3.1 Sampling of Rhizosphere Soil and Solution

3.1.1 The Straightforward Root-Shaking Approach: Sampling the Soil Adhering to the Roots

The simplest technique for collecting rhizosphere soil samples was first described and used by Riley and Barber [83]. To our knowledge, it was the first convincing report of significant pH changes occurring in the rhizosphere. At plant harvest, these authors carefully separated the roots plus adhering soil from the bulk of the soil. They discarded the portion of soil that was weakly adhering to the roots (as removed by gentle shaking) and considered as rhizosphere (“rhizoplane”) soil the portion that was strongly adhering to the roots (and roughly 0 to 2 mm from the root surface). The soil pH was then measured in a conventional way for both types of samples. They applied this technique successfully to show significant pH changes occurring in the rhizosphere of soybean (*Glycine max* L.) in relation to the form of nitrogen supplied. This technique has been applied for sampling rhizosphere and bulk soil in both pot and field experiments for crops [83–85], trees [86–89], and other wild plants [90]. Several of these studies showed significant changes of pH occurring in the rhizosphere relative to the bulk soil.

A major limitation of this rather straightforward approach is the possibly poor representativeness of the so-called rhizosphere or rhizoplane soil. Indeed, the method of separation of rhizosphere and nonrhizosphere soil provides an operational but rather arbitrary distinction. The amount of soil strongly adhering to the roots indeed depends much on physical properties of the interface such as soil texture, humidity, concentration of mucilage, or root hairs, i.e., properties that may vary with soil type, plant species, root type or root portion, etc. It should also be stressed that sampling the rhizosphere soil adhering to fine roots is even harder. In addition, the spatial extension of the rhizosphere in terms of pH change is likely to be different (larger or smaller) from the spatial extension of the strong adhesion that roots can exert to soil particles, leading to biased results. When this technique is directly applied in situ, especially for natural ecosystems, another major difficulty is to make a clear distinction between a true rhizosphere effect and artifacts due to the initial heterogeneity of the soil that plant roots may exploit when colonizing the soil [90]. The results obtained with this technique thus need to be interpreted cautiously, particularly when applied to undisturbed soil (for in situ measurements).

3.1.2 The Root Mat Approaches

An alternative technique for sampling rhizosphere soil is derived from the early work of Farr et al. [91], who first grew a dense, planar mat of roots against a volume of soil that was ultimately sliced parallel to the mat of roots in order to col-
lect soil samples at various distances from the roots. These authors showed a marked depletion of K ions and an increase in H⁺ concentrations in the vicinity of the roots of onions (*Allium cepa* L.). The technique was further refined by Kuchenbuch and Jungk [92], who inserted a nylon mesh between the roots and the soil to avoid penetration of the roots into the soil during the experiment [93]. Such a technique and its many derivatives, sometimes called rhizoboxes, were successfully used by many authors to show significant changes in pH occurring near plant roots and to determine the spatial extension of these rhizosphere processes [93–99]. With this approach, significant changes in pH of up to more than one pH unit were demonstrated to occur and extend over one to several millimeters, with a typical H⁺ diffusion pattern (Fig. 6).

However, this technique has been criticized because of the unrealistic (planar) geometry of the rhizosphere it provides and because of the subsequent risks of overestimating the intensity and spatial extension of rhizosphere processes compared with a radial geometry [100]. In addition, the soil slicing procedure is tedious and needs to be achieved as quickly as possible after the removal of the root mat to avoid a redistribution of ions, including H⁺/OH⁻, during the procedure [93]. To avoid the need to slice a soil column and to compare large numbers of treatments and/or replicates, the technique can be simplified by using a thin layer of soil (2 to 3 mm) in contact with the mat of roots [101–103]; this soil layer could be considered the rhizosphere soil, based on the spatial extension of rhizo-

**FIGURE 6** Profiles of pH in the rhizosphere of ryegrass grown in a luvisol and supplied with NH₄⁺ (+) or NO₃⁻ (○). The data were obtained using the root mat approach. (Redrawn from Ref. 96. Copyright 1992, Kluwer Academic Publishers, Netherlands).
sphere processes as previously reported in the literature. This technique can illustrate significant pH changes occurring in the rhizosphere, relative to unplanted pots of similar geometry and incubated in a similar manner [103]. Another approach in which plant roots are grown directly in the thin layer of soil sandwiched between two glass slides is based on similar basic assumptions: once a sufficient density of roots have colonized the soil, the whole of it can be considered the rhizosphere [104]. This experimental device that is easy to set up and handle was successfully used to show dynamics of rhizosphere pH [105, 106].

3.1.3 Approaches Designed for Sampling Defined Root Zones

All the previously described approaches are destructive in essence. They enable collection of large amounts of rhizosphere soil for making soil pH measurements in a usual manner (with a conventional electrode) and even simultaneously carrying out other measurements of physicochemical or biological properties of the rhizosphere. This is, however, achieved by bulking up the rhizosphere material collected for the whole root system of a single plant or a group of plants. Therefore, another major limitation of these approaches is that they do not give access to the spatial heterogeneity of pH changes that are known to occur along the root system (see Secs. 2.3.2 and 2.3.3). To assess this spatial variability, several authors have used rhizotrons that allow visualization of the distribution of the root system at the soil surface and collection of small samples of rhizosphere soil around given portions of the root system [107–109]. However, these procedures are tedious and their reproducibility on a large scale is rather questionable. In addition, given the small amounts of soil that can be collected in that way, microprocedures of sampling and analysis needed to be designed. For instance, an immiscible displacement–centrifugation technique was proposed to enable the collection of the soil solution from rhizosphere soil samples of less than 6 [107].

Göttlein et al. [110, 111] proposed an alternative approach to collecting small volumes of soil solution at defined locations along the root system. This technique was based on the use of an array of microsuction cups that were inserted in the vicinity of roots grown in rhizotrons (Fig. 7). It enabled the measurement of the pH and ionic concentrations in small volumes of soil solutions that were collected at various time intervals during plant growth by applying suction to the microsamplers [110–112]. This approach therefore provides a unique, nondestructive method for sampling the rhizosphere soil solution and for measuring the pH changes at defined locations along the root system.

3.2 Use of pH Dye Indicators in the Rhizosphere

The simplicity of using the agar-indicator technique described in Sec. 2.3 has led several authors to adapt it to field conditions for convenient estimation of the root-
induced pH changes under natural conditions [113–122]. However, the principle of the technique has considerably limited such developments. This approach was initiated by Marschner and Römheld [113]. It was based on using an agar film that included the pH indicator to obtain the pH map in the rhizosphere in a manner similar to the use of a photographic film in autoradiography. Plants were grown in rhizotrons that were slightly inclined so that roots preferentially grew against the front glass slide. Thin agar sheets that included the indicator were molded and cooled separately. For measuring the rhizosphere pH, the front glass slide of the rhizotron was removed and replaced by the agar sheet. The H⁺ diffused from the soil solution into the agar sheet, causing a change in the color of the indicator and hence revealing the rhizosphere pH within a few minutes. The method produced valuable results when the pH changes were large enough to induce consequent color contrasts. The results were dependent on the type of soil used, light-colored soils being more suitable than dark ones.

The agar-indicator technique has been used especially by authors who studied the release of H⁺ by tree roots because these roots are too rigid to be laid onto an agar sheet, as opposed to roots of herbaceous plants. The use of a premolded agar sheet laid onto roots grown against a glass slide made it possi-

FIGURE 7 Experimental device for sampling the soil solution in the rhizosphere of a tree seedling with an array of microsuction cups. (Redrawn from Ref. 110. Copyright 1996, Elsevier Science, Ireland).
ble to overcome such experimental difficulties. Häussling et al. [114] and Marschner et al. [115] were thereby able to study the behavior of roots of 4-year-old Norway spruce (*Picea abies* L. Karst.) grown in pot experiments as well as those of a 60-year-old Norway spruce grown in a forest stand. These data are among those obtained with the oldest plants grown in natural conditions. Studying the nitrogen nutrition of Douglas fir (*Pseudotsuga menziesii*) and the consequent \( \text{H}^+ \) release by roots, Gijsman [86,121] simplified the procedure by using only small strips of agar to cover given portions of the roots from place to place. The principle remained the same: aiming to explore the root behavior in situ in field conditions. It should be stressed that the use of the agar-indicator technique was combined with local measurements of pH using microelectrodes [114–121]. The microelectrodes were carefully inserted into the agar sheet in the rhizosphere soil or in the immediate vicinity of root surface. The agar sheet provided a moist environment in the rhizosphere and prevented the drying out of both soil and roots during the course of the measurement, thereby improving the reliability of the pH values obtained.

All the previous studies were achieved in very acid soils whose bulk pH was below 5.0 or even 4.0. In such conditions, it appeared that pH near the root surface increased at the root tips and decreased farther away from the tip relative to the bulk soil pH. The pH increased especially when nitrogen was supplied as nitrate. The reported pH changes were substantial in such acidic conditions and might have contributed to modifying significantly the physicochemical dynamics of elements such as aluminum or the microbial activity in the rhizosphere. However, the results obtained with this method remained qualitative in essence, and only the combined use of quantitative techniques such as pH microelectrodes made it possible to assess the actual pH values in the rhizosphere.

### 3.3 Use of pH Microelectrodes in the Rhizosphere

The most direct method for measuring \( \text{H}^+ \) activity is potentiometry (see Sec. 2.2). However, few scientists have been using this method for measuring rhizosphere pH because of the experimental difficulties encountered in the soil and especially in situ in field conditions. In fact, soil is a medium that is definitely not suitable for using fine probes such as pH microelectrodes. First of all, it is opaque, which raises the problem of properly positioning the probe. Either blind positioning of probes or rather destructive positioning of the probes is needed to access the most relevant sites. In addition, sturdy probes are needed to penetrate into the soil because of mechanical constraints. Finally, soil is a rather dry medium, which raises the problem of liquid continuity between the probe and the soil. These reasons explain why only a few scientists used potentiometry for measuring the rhizosphere pH, but they nevertheless produced some remarkable results.
3.3.1 The Criticized but Sturdy Antimony Microelectrodes

A major step forward in using microelectrodes for measuring rhizosphere pH has been accomplished by Schaller and Fischer [123–128], who underlined that glass electrodes were unsuitable for long-term pH measurements in microsites in soil because of their shape and size and because of the drying of the glass membrane [123]. They therefore developed microelectrodes based on antimony oxidoreduction in water, which can be described by the following equations [123,129]:

\[
\text{Sb(s)} \rightleftharpoons \text{Sb}^{3+} + 3e^- \quad (10)
\]

and

\[
\text{Sb}_2\text{O}_3(s) + 6\text{H}^+ + 6e^- \rightleftharpoons 2\text{Sb}^{3+} + 3\text{H}_2\text{O}(l) \quad (11)
\]

Combining these two redox half-reactions (10) and (11), the result is

\[
\text{Sb}_2\text{O}_3(s) + 6\text{H}^+ \rightleftharpoons 2\text{Sb}^{3+} + 3\text{H}_2\text{O}(l) \quad (12)
\]

Because they are based on a solid surface reaction, the electrical impedance of antimony microelectrodes is lower than that of glass electrodes; therefore, their tip may be easier to miniaturize. Moreover, they are sturdy, easy to build, and may be used conveniently in a wide range of conditions. Microelectrodes were constructed by sucking melted antimony into preheated glass capillary tubes less than 1 mm in diameter [114–116,123–126]. After cooling, the antimony bar was extruded and fastened in a Pasteur pipette that had been formerly insulated with waterproof plastic. Finer tips were obtained by melting together antimony and a glass capillary that had been especially selected for its melting temperature [130].

This simple and cheap method for building antimony microelectrodes has made it possible to produce a large number of them. Fischer et al. [128] constructed regular arrays of microelectrodes inserted in rhizotrons to monitor the root-induced pH changes in the rhizosphere of growing roots (such as the device showed in Fig. 7). The quantitative data obtained in these experiments that were conducted over several days in different soils confirmed numerous previous observations made with plants cultivated in hydroponics and also pointed out the peculiar role the soil played in rhizosphere pH changes. They showed, for instance, that the root activity of groundnut (\textit{Arachis hypogea} L.) and consequent pH change in the rhizosphere develop cyclically according to a diurnal cycle: in a loam soil at pH 5.0, the rhizosphere pH fluctuated between 5.0 and 3.5–3.8, depending on the exposure of plants to light. With the same plant species grown in a brown soil at pH 5.5 fertilized with \textit{NH}_4\textsuperscript{+}, the pH values in the rhizosphere decreased to less than 3.0 within a single day [124]. When investigating the positions of the electrodes relative to the root tip, it was confirmed that the pH change was maximum between 1 and 3 cm behind the tip (a drop of up to 2.5 pH units), with an average decrease of around 2.0 pH units along the mature parts of the roots.
In an alkaline soil at pH 7.8, rhizosphere pH decreased with NH₄⁺ and increased with NO₃⁻ supply, but the intensities of pH changes were much lower than those mentioned previously for an acid soil because of the large buffering capacity of the alkaline soil. In very acid soils at pH 3.2, rhizosphere pH increased up to 4.0 within 1 day, as reported for tree roots grown in natural conditions and fed with nitrate [86,114,121].

The same experimental device using an antimony microelectrode array also made it possible to evaluate the effect of H⁺ released by roots in determining the extent of spatial extension of pH changes in the rhizosphere in terms of the radial distance from roots [124–127] (Fig. 8). The H⁺ buffering capacity of soils is generally higher than that of soil solution because of the ability of the soil solid phase to react with H⁺ (1) via cation exchange reactions, (2) via protonation/deprotonation of weak acid groups on soil constituents, and (3) via dissolution or precipitation of soil minerals (reactions that respectively consume or produce H⁺).

Schaller and Fischer [126] showed that, after acid addition, the H⁺ activity in soil solution steeply increased first, then slightly decreased for several hours before reaching equilibrium. Investigating the influence of soil pH buffering on the extension of rhizosphere pH changes, Schaller [127] showed that the pH change induced by roots was strongly and linearly correlated with the short-term buffering capacity of the soils as determined 5 minutes after acid addition (when measured in soil suspensions). This suggested that the pH profile around roots, and thus the

**Figure 8** Profiles of pH as a function of the distance from the surface of a single root of groundnut grown in rhizotron. The data were measured after 20 (▲), 30 (●), and 60 hours (○) using antimony microelectrodes. (Redrawn from Ref. 124. Copyright 1985, Wiley-VCH, USA).
extension of pH changes in the rhizosphere, resulted from dynamic interactions between continuous H⁺ release by the growing roots and H⁺ uptake by the buffering solid phase of the rhizosphere. In the studied soils, the extension of pH changes in the rhizosphere of groundnut was 2 mm on average: it was largest in soils with an initial pH of 5.5 (2.8 mm) and smallest (1.4 mm) in more alkaline and acidic soils, which was in good agreement with theory [6].

Fischer and Schaller [131] had formerly built an array of platinum microelectrodes for measuring redox potential in the rhizosphere. Using combined arrays of antimony and platinum microelectrodes (matrices made of 30 to 50 electrodes), these authors [128] successfully measured simultaneous changes in pH and redox potential in the rhizosphere of faba bean (Vicia faba L.) They thereby monitored the evolution of rhizosphere pH and Eh over time periods of 3 to 4 days (Fig. 9). Measurements near a growing root showed a rapid drop of both pH and Eh for about 1.4 pH units and 330 mV, respectively. Changes in redox potential and pH are not independent; indeed, a reduction process is expected to be accompanied by a pH increase [5], whereas a net pH decrease was reported in the present case. This pH change can be explained to a large extent by the cation–anion balance at the root–soil interface, whereas the decrease in redox potential was attributed either to root and microbial respiration or to the exudation of reducing compounds by plant roots [128].

Antimony microelectrodes have severe limitations that restrict their practical use to defined experimental conditions. The main limitation is their sensitivity to several environmental factors, such as the concentrations of oxygen and carbon dioxide and those of organic anions such as citrate or oxalate. For instance, in controlled conditions, the measured pH increases when pO₂ decreases [123] or citrate concentration increases [123,129]. On the one hand, the interference with oxygen results from the possibility to form a range of antimony oxides other than the main trioxide, which ultimately influences the electrode potential for a given H⁺ concentration in solution. On the other hand, carbon dioxide and organic anions may form some complexes at the surface of the solid and also influence the electrode potential. In addition, the pH measured with the antimony microelectrode decreases with decreasing soil water content, and glass electrode measurements do not detect any change in soil pH [123,132]. All these environmental factors are likely to vary strongly in the rhizosphere [3]. The use of antimony microelectrodes therefore requires much caution to obtain reliable pH measurements. These microelectrodes should thus be kept only for experiments in controlled and steady-state conditions.

3.3.2 The pH-Sensitive Glass Microelectrodes

The glass membrane electrodes are undoubtedly the most selective and sensitive probes to measure the H⁺ activity in soil and solution. Unfortunately, they have numerous limitations for use in soil conditions: (1) their large electrical...
impedance requiring a large membrane area, (2) the necessity to prevent the glass membrane from drying, and (3) their particularly frustrating fragility. As previously pointed out, glass microelectrodes have, however, been occasionally used to complement other methods, such as the agar-indicator technique in soil [86,121,133]. However, the glass membranes of the electrodes used in these studies were about 2 mm in diameter, which makes them inappropriate for local measurements in the rhizosphere.

FIGURE 9 Evolution of pH (a) and Eh (b) at different positions in the rhizosphere of faba bean over several days of growth. The data were obtained using a grid of antimony (for pH) and platinum (for Eh) microelectrodes. The changes in pH and Eh occurred when the growing root approached the microelectrodes. The antimony microelectrodes E₁ and E₂ were near the platinum microelectrodes F₁ and F₂, respectively. (Redrawn from Ref. 128. Copyright 1989, Wiley-VCH, USA).
In the meantime, plant and animal physiologists have been developing liquid and glass membrane microelectrodes with tips as small as 1 μm or even less (see Sec. 2.2). After having used antimony microelectrodes [129,134], Blanchar and coworkers [135,136] designed a novel generation of glass microelectrodes that were both sturdy enough to be used in soil conditions and thin enough to allow pH measurements in soil microsites, i.e., small enough relative to rhizosphere dimensions. The basic idea was to strengthen the sensing tip in order to stand moderate physical constraints without damage. The design was an inner insulated pipette inserted into a sealed pH-sensitive glass tip 10 to 20 μm in diameter, the whole lot being inserted in a glass support [135]. The microelectrode construction and calibration for pH measurements in soil were later improved [136]. Because of the sensitivity of microelectrodes to electrical interference, the entire measurement device needed to be insulated and grounded to a Faraday cage.

These pH-sensitive glass microelectrodes have been used for measuring pH in the rhizosphere of plants growing in different conditions [78,137,138]. For instance, Conkling et al. [137] studied the effect of acidity applied to the shoots of corn (*Zea mays* L.), alfalfa (*Medicago sativa* L.), and soybean (*Glycine max* L.) to simulate acid rains. Plants were grown in rhizotrons filled with acidic soil ranging in pH from 4.2 to 6.5. They showed that rhizosphere pH change was linked to acidification (except for alfalfa grown at pH 5.5). Moreover, the reported pH drop increased with the initial bulk pH: with corn it was nil at pH 4.0 and reached on average 0.75 pH units at pH 6.0, and with soybean it was also nil at pH 4.0 and reached 1.35 pH units at pH 6.0. In spite of the poor nodulation of soybean roots, soybean decreased the rhizosphere pH to a greater extent than corn. In addition, the pH change was greater near neutrality than in acidic conditions, which was in good agreement with theory [6]. It should be borne in mind, however, that pH 4 is already a very acidic pH for plants.

These results were confirmed by measuring the rhizosphere pH of field-grown soybean [138] (Fig. 10). The prime objective was to evaluate the influence of the thickness of the soil surface horizon on root growth and rhizosphere pH. Soil–root cores were sampled in the field, frozen, and brought back to the laboratory for further measurements. They were then thawed and dissected carefully to display the roots and surrounding soil. Soil pH was measured with a glass micro-electrode at 0.5 and 5 mm from the root surface, the sensing tip (20 μm in diameter) being inserted to a depth of about 100 μm into the soil. This procedure was repeated at three time intervals. The method of freezing and thawing of the soil–root cores might be criticized because of the potential artifacts it could have generated by inducing a release of the root cell content, for instance. However, the results obtained with this method were consistent and in agreement with other studies. They showed that pH in the rhizosphere of soybean was always lower than bulk soil pH. The pH change was correlated with the initial pH of the bulk soil: almost nil for a bulk pH of 4.0 and increasing (in absolute value) with increasing
bulk pH (Fig. 10). This result is consistent with the data obtained using antimony microelectrodes [127] and with the theory, which shows that the buffering capacity of a soil solution is lower near neutrality [6]. In addition, these results showed that, for a given sampling time, the pH values in the rhizosphere of lateral roots were lower than those in the rhizosphere of the primary roots (Fig. 10). Above all, following several field studies [85, 88–90, 114, 116], this work definitively demonstrated that the pH around roots of field-grown plants can be significantly different from the bulk soil pH. This should be taken into account for better understanding plant growth and plant nutrition in soils in the field.

The use of pH-sensitive glass microelectrodes is restricted because they are not commercially available and require technical expertise to be properly built. In addition, the mechanical fragility of the sensing tips is a major limitation for their use. The results presented here showed that this difficulty can be overcome. More data should therefore be obtained with this technique in the future, in particular from in situ measurements of rhizosphere pH in field conditions. Generally speaking, the potentiometric methods may potentially give access to other significant soil parameters such as specific ion activities. The technique of microelectrodes based on a glass membrane or liquid membrane consolidated with polyvinyl chloride [139], which has already been considerably improved, is likely to lead to further advances in this area. These microelectrodes should help to make another step

**Figure 10** Changes of pH in the rhizosphere of lateral (●) and primary (□) roots of soybean after 55 days of growth in field conditions versus bulk soil pH. The data were measured in the laboratory using pH glass microelectrodes. Bulk soil pH was the pH of soil at 5 mm from the root surface. (Redrawn from Ref. 138. Copyright 1996, Soil Science Society of America Inc., via Copyright Clearance Center, USA).
forward in the measurement of physicochemical conditions and associated fluxes of ions in the rhizosphere and other soil microsites.

4 CONCLUSIONS

Plant-induced pH changes were reported in the 19th century. In his treatise on agricultural chemistry, Dehérain [140] reported an experiment conducted by Sachs in 1860 that demonstrated that rootlets can secrete an acid powerful enough to dissolve calcium carbonate; this experiment was reproduced later by other authors [141], who showed etched traces of roots grown on the surface of a marble plate. In addition, in 1894, when designing a method for measuring plant available phosphorus, Dyer [142] selected citric acid as an extractant that would best mimic the acids supposedly produced by roots. However, these root-induced processes were then ignored for a long time, and almost nothing dealing with root-induced pH changes is to be found again in the literature prior to the 1970s.

Considerable progress has been achieved since the 19th century, and mostly over the last two decades, through the development of a range of techniques for measuring the fluxes of $\text{H}^+$ released by roots and the resulting rhizosphere pH. The most remarkable achievements have been obtained in vitro, in rather artificial, controlled conditions. The development of techniques such as pH-stat systems and micropotentiometry designed for solution culture experiments has helped ascertain the physiological origins of root-induced pH changes (e.g., root elongation, mineral nutrition, cation–anion balance, responses to environmental stresses such as wounding, deficiencies, or toxicities). The use of dye indicators has also helped provide evidence for the functioning of different parts of the whole root system of a single plant. In natural conditions, the available data on pH changes induced by roots in situ are, however, much less numerous, mostly because of lack of appropriate methods.

In acid soils, root-induced pH changes are of prime importance. Indeed, aluminum is a toxic element that severely limits growth at pH below 5.0 as a consequence of its pH-dependent speciation and the considerable increase in the solubility of aluminum-bearing minerals with decreasing pH. Under such acidic conditions, a further decrease in rhizosphere pH would lead to root intoxication by Al and impairment of plant growth. Several authors [13,143–147] have shown that the tolerance to soil acidity and Al toxicity in certain species or genotypes was related to their ability to take up $\text{H}^+$ and thereby to increase rhizosphere pH. Better knowledge of the $\text{H}^+$ fluxes in and out of roots in acid soils in field conditions might improve our understanding of plant adaptation to such adverse environments. Knowing their intensity, direction, and location along the roots and understanding the factors that determine these fluxes would provide the base to improve plant growth in acid soils.
REFERENCES


75. V Römheld. pH-Veränderungen in der Rhizosphäre in Abhängigkeit vom Nährstoffangebot. In: H Kick, M Kirchgessner, HJ Osłage, U Ruge, E Schlichting, O Siegel,
H⁺ Flucts and Concentrations in the Rhizosphere

146. WG Keltjens. Plant adaptation and tolerance to acid soils; its possible Al avoidance-
A review. In: AC Moniz, AMC Furlani, RE Schassert, NK Fageria, CA Rosolem, H
Cantarella, eds. Plant–Soil Interactions at Low pH. Campinas, Brazil: Brazilian So-
147. J Degenhardt, PB Larsen, SH Howell, LV Kochian. Aluminum resistance in the
Arabidopsis mutant alr-104 is caused by an aluminum-induced increase in rhizo-
1 INTRODUCTION

Soils are identified as being “acid” by their low pH, although H⁺ per se is rarely the limitation to plant growth. Jenny [1] perceived that, during the 25 years that preceded his review in 1961, soil acidity research had come full-circle, from the identification by Veitch [2] that acid clays were Al clays to the 1960s interest in solution chemistry and exchange behavior of Al. Jenny felt that agronomists, who had once thought that plants in an acid soil were confronted by H⁺ ions, had received a new stimulus with the recognition of Al toxicity as a limitation to plant growth in acid soils. He conjectured that “Presumably the plants knew this all along.” Forty years after Jenny’s review, the challenge to soil researchers remains the same, namely to identify which of the many potential effects of soil acidity is limiting plant growth.

Acid soil infertility is a complex interaction of growth-limiting factors. Plant growth may be restricted by one or more of the following: low pH; Al or Mn toxicity; Ca, Mg, P, or Mo deficiency; and reduced mineralization, nitrification, nodulation, and mycorrhizal infection [3]. Such effects are not confined to surface soils. Subsoil acidity may adversely affect plant growth, persistence through restricted depth of root proliferation, and nutrient and water uptake. This chapter
deals primarily with the phytotoxic elements H, Mn, and Al. It addresses the effects of these toxic elements on plant growth, where appropriate the specific form of the element that is toxic, and the use of soil tests to identify situations in which these elements will limit plant growth.

2 SOIL PH

2.1 The Phytotoxicity of H⁺

In soil culture, the direct assessment of the effects of H⁺ is precluded by the confounding effects of Al and/or Mn released by mineral dissolution at low pH. However, studies conducted in solution culture have clearly demonstrated that H⁺ can limit plant growth. Islam et al. [4] observed root injury in six crop species at pH 3.3 and pH 4.0 but not at pH 4.8. Blamey et al. [5] reported within-species differences in response to H⁺ for sunflower (Helianthus annuus L.), with critical solution pH (90% maximum total dry matter yield) for four cultivars ranging from pH 3.9 to pH 4.5. A solution pH of 3.5 was found to be lethal to all four cultivars tested. Excess H⁺ ions have a marked effect on membrane structure and function. Foy [3] cited examples of reduced uptake of Ca, Mg, Mn, Zn, Cu, and P and loss of organic substances and nutrient ions by H⁺-damaged roots. Although H⁺ is directly detrimental to plants, in low pH mineral soils the adverse effects of Al and/or Mn toxicity generally considerably outweigh the adverse effect of H⁺.

2.2 Measurement of pH

Soil pH is regarded as a controlling variable in soil systems, influencing ion exchange, solubility, adsorption, redox, and complexation reactions. It is undoubtedly the measurement most commonly made on soils. Measurements of soil pH are generally made by determining the electrical potential difference between a glass membrane electrode, which is responsive to H⁺ activity, and a reference electrode that generates a known and constant potential. The electrical circuit is completed through a salt bridge that permits ions to diffuse from the internal solution of the reference electrode to the external solution. The selection of an appropriate salt for the internal solution in the reference electrode is critical, as an unbalanced diffusion of anions and cations across the salt bridge would produce a junction potential. Concentrated KCl is typically used as a reference electrode filling solution as K⁺ and Cl⁻ have almost identical mobilities; thus, the junction potential should be small [6]. In soil suspensions, the effects of charged colloids on the mobility of ions disrupt this ideal behavior, leading to the development of higher junction potentials in soil suspensions than in clear solutions. Published procedures for pH determination differ widely in their treatment of this issue, with methods recommending placement of the glass electrode and salt bridge in the supernatant, placement of the glass electrode in the suspension and salt bridge in the
supernatant, and measurement in a constantly stirred solution. The critical issue is that the measurements be made in a consistent way [7].

The pH of soil suspension is influenced by the ratio of soil to solution, with 1:1, 1:2, and 1:5 ratios all commonly used. In soil suspensions the pH is buffered by dissociation of H⁺ from the soil surface and hydrolysis of Al [7], maintaining a relatively stable pH with dilution. Nevertheless, the amount of hydrolyzable acidity is finite and the pH tends to increase as the suspension is diluted. Furthermore, dilution reduces the displacement of Al³⁺ and H⁺ by soluble salt cations, contributing to the increase in measured pH with dilution.

The pH is also dependent on the salt content of the measuring solution. A criticism of pH measured in deionized water suspensions is that seasonal change in a soil’s soluble salt content or the addition of neutral salt fertilizers can lead to changes in the measured pH. The measurement of pH in salt solutions such as 0.01 M CaCl₂ or 1 M KCl has been advocated to suppress this effect [8]. However, this approach confounds explicit acidity (proton or active) with latent acidity (proton generating or reserve). Furthermore, the use of salt solutions will mask the “real” pH changes that can result from the addition of neutral salts. The impact of neutral salts on soil acidity is well demonstrated by the reduced soil solution pH and increased Al toxicity that can result from the application of gypsum to soils [9].

The use of a concentrated salt solution to measure pH results in displacement of Al³⁺ and H⁺ from exchange sites and the deprotonation of variable charge sites on organic matter and mineral surfaces. Thus, the suspension pH will be artificially lowered. In contrast, an unequivocal estimate of active acidity is provided by a measurement of soil solution pH. This is the pH condition encountered by plant roots and that at which reactions occur in the soil. Thus, the most appropriate medium for measuring soil pH would be one that best simulates the characteristics of the soil solution [10]. Gillman [11] suggested that measurement at an ionic strength of 0.005 M would be appropriate for tropical soils on the basis of the low ionic strength of their soil solution. The effectiveness of pH measurement in a dilute salt solution was demonstrated for 90 soils from eastern Queensland by Aitken and Moody [12], with a 1:5 soil/0.002 M CaCl₂ suspension providing the closest approximation to the soil solution pH.

3 MANGANESE

3.1 Manganese as a Plant Toxin

Manganese is an element essential for plant growth, but it becomes detrimental when the supply to the plant is excessive. Manganese is readily taken up and transported from roots to shoots [13]. This probably accounts for the early appearance
of Mn toxicity symptoms on shoots. It is generally accepted that Mn(II) is the prevailing source of Mn for plant uptake. Critical Mn concentrations in the range of 0.2 to 12 mM have been reported to produce severe growth limitations in solution culture studies of species such as cotton (Gossypium hirsutum L.) [14], sweet potato (Ipomoea batatas L.) [15], sorghum (Sorghum bicolor) [16], and wheat (Triticum aestivum L.) [17]. In contrast to these studies conducted in high-ionic-strength solutions, critical values one to two orders of magnitude lower have been obtained from low-ionic-strength systems more representative of conditions in soil solutions [18]. Dilute flowing solution culture studies have shown that critical external Mn(II) concentrations for toxicity (90% maximum whole plant yield) vary widely among plant species, with wheat and corn (Zea mays L.) relatively sensitive (critical concentration 1.4 μM) and sunflower particularly tolerant (critical concentration 65 μM) [19]. For cowpea (Vigna unguiculata L.), Taylor et al. [20] observed toxicity symptoms at 0.5 μM Mn, with a 25% reduction in growth at 1.0 μM Mn.

Despite the use of solution conditions comparable to soil solution, direct translation of solution culture values to soil culture is precluded by the capacity of plants to alter conditions within their rhizosphere. Certain Mn-tolerant varieties of wheat, barley (Hordeum vulgare L.), rice (Oryza sativa L.), peas (Pisum sativum L.), and corn increase the pH of their rhizosphere [21], decreasing the Mn availability. The superior Mn tolerance of rice over soybean (Glycine max Merr.) is attributed to the capacity of rice roots to oxidize Mn from the soluble divalent to relatively insoluble trivalent form, decreasing uptake by the plant [22]. Doi [22] found that soybean was injured by Mn if planted alone in paddy soils, but the extent of injury was reduced if rice was planted with soybean. The beneficial effect was probably due to the decreased soil solution Mn(II) concentration as a result of Mn oxidation and precipitation in the rice rhizosphere. In contrast, to the oxidizing nature of the rice roots, conditions in the rhizosphere of most plants are likely to favor the reduction of Mn to the soluble divalent form [23]. The plant’s influence on the rhizosphere means that the condition of the bulk soil may provide a poor indication of the Mn concentration at the root surface.

Expression of Mn toxicity is markedly affected by the supply of other nutrients. A protective effect of Si has been widely reported, although the means by which this effect is mediated is not clear [24]. The severity of Mn toxicity is inversely related to the supply of Ca and Mg, and both positive and negative interactions with the supply of Fe have been reported [24]. Plants supplied with N as NO₃ develop Mn toxicity symptoms and have higher tissue Mn concentrations than plants supplied with NH₄ [25,26]. Plants supplied with NO₃ tend to raise the pH of their rhizosphere [27], decreasing the solubility of Mn; thus, the increased Mn uptake where NO₃ is supplied is clearly not the result of N supply–induced rhizosphere pH change.
3.2 Solution Chemistry of Mn

Manganese (II) is the only oxidation state of Mn expected in appreciable concentrations in solution within the pH and pe ranges found in soils [28]. Higher oxidation state Mn(III) and Mn(IV) are considered too reactive to persist in soil solution, although Mn(III) may be present as an intermediate in soil redox reactions [29]. Complexing ligands can stabilize Mn(III) in solution temporarily, but disproportionation of Mn(III), oxidative decomposition of the associated ligand, and low solubility of Mn(III) and Mn(IV) oxides limit the persistence of Mn(III) complexes in solution [29].

Fully hydrated Mn$_2^{2+}$ is the dominant inorganic Mn species in soil solutions and natural waters. Ion pairs with SO$_4^{2-}$, HCO$_3^-$, and Cl$^-$ are formed but would be present only at activities equal to that of Mn$_2^{2+}$ where the anions are present at activities of 0.005, 0.016, and 0.25 M, respectively [28]. Of the three anions, only sulfate is likely to be encountered in acid soils at activities of this magnitude [18].

Complexation of Mn(II) by a range of organic ligands is possible [30]; however, the stabilities of Mn(II) complexes are too low for Mn$_2^{2+}$ to compete effectively with relatively abundant cations such as Ca$_2^{2+}$ and Mg$_2^{2+}$ [30]. This prediction has generally been supported by studies of soil solution composition. In an acid sandy loam soil, Sanders [31] found that organic complexation of Mn increased from 10% as the pH was raised by liming, reaching a maximum of 65% above pH 7. In six flooded soils, Olomu et al. [32] found that 25 to 40% of soil solution Mn was retained by an anion exchange resin, whereas 100% was retained by a cation exchange resin, suggesting that some form of labile, organically bound Mn was present. In marked contrast to these studies, Geering et al. [33] reported organic complexation of 84 to 99% of the Mn in the soil solutions from 13 topsoils of widely differing pH and texture.

3.3 Identification of Mn-Toxic Soils

Whereas the form of Mn available to plants is well known and is readily quantified by routine analytical methods, the accurate determination of the concentration of Mn to which plant roots are exposed remains problematic. This arises in part from the effects of roots on conditions in their rhizosphere but is also the result of the complex behavior of Mn in soil systems. The simplest representation of Mn reactions in soil can be given as [34]

\[
\text{Root} \xleftarrow{\text{Uptake}} \text{Mn}^{2+} \xrightarrow{\text{Ox.}} \text{MnO}_x \xrightarrow{\text{Red.}} \text{MnO}_x
\]

where Mn$^{2+}$ can be oxidized by soil microorganisms to insoluble oxides MnO$_x$ (where $1 < x < 2$). Even in aerobic soils, MnO$_x$ is continuously being reduced to Mn$^{2+}$ by soil organic matter. The balance between these reactions in soil is one of quasi-equilibrium because the forward and reverse reactions are somewhat inde-
ependent of one another and may be separated spatially. At any point in time, the concentration of water-soluble plus exchangeable Mn is determined by the relative rates of oxidation and reduction [34]. This complex field condition can easily be disturbed by soil sampling procedures and is drastically altered by air drying the soil [35].

Various extractants have been used to assess soil Mn, with dilute extractants generally found to be most effective. Water extracts (1:2 and 1:5) have been correlated with the growth of lespedeza (Lespedeza striata Thunb.), King Island melilot (Melilotus sp. Mill.) [36], and kikuyu (Pennisetum clandestinum) [37] and found to be more effective than measures of exchangeable Mn or reducible Mn in predicting Mn toxicity in cotton [38]. Extraction with 0.01 M CaCl₂ was a more effective predictor of Mn uptake by barley, turnip rape (Brassica campestris L.), alfalfa (Medicago sativa L.) [39], subterranean clover (Trifolium subterraneum L.), and switchgrass (Panicum virgatum) [40] than methods intended to assess acid-soluble, exchangeable, or reducible Mn [40,41].

Soil solution Mn concentration has been strongly correlated with plant Mn uptake in studies in which solution was extracted directly from field-moist soil [40,42,43]. However, where soil was air dried and then rewet prior to soil solution extraction, the effectiveness of soil solution Mn concentration as a predictor of plant Mn uptake was low [44]. In a study of Mn uptake by rice in acid sulfate soils, Moore and Patrick [42] found plant uptake of Mn more closely correlated with p(Mn/Fe) than with Mn²⁺ activity, confirming the Mn/Fe interaction reported in solution culture experiments [24].

Soil testing to identify Mn toxicity has not been widely adopted, and few critical values have been published. Hoyt and Nyborg [41] proposed the use of 0.01 M CaCl₂ as an extractant for Mn and subsequently refined the extraction procedure [45,46] but did not report critical values. The Hoyt and Nyborg extractant, 0.01 M CaCl₂, is increasingly being adopted as a test for Mn toxicity and a number of critical values have been published: rape (Brassica napus L.) > 20 mg kg⁻¹, subterranean clover > 50 mg kg⁻¹ [44], poppy (Papaver somniferum) two sites > 5.1 and > 0.5 mg kg⁻¹ [47], barley, wheat, and triticale (Triticum × Secale) < 10 mg kg⁻¹ nonlimiting [48]. Direct comparison of these critical values is precluded by the wide variation in sample treatment between studies; some samples were analyzed in the field-moist state while others were air-dried or oven-dried at 40°C. These differences in sample treatment will alter the Mn chemistry of the sample and change the soil test critical value obtained [35].

Additional difficulties in establishing critical values for Mn toxicity arise from the confounding effects of Al toxicity in acid soils. This effect was well demonstrated by the data of Hoyt and Nyborg [45], who found that for 40 acid soils, the Mn content of a 0.02 M CaCl₂ extract was strongly correlated with Mn uptake by barley, rape, and alfalfa (correlation coefficients of 0.75, 0.84, and 0.83, respectively) but poorly correlated with plant yield (partial regression coefficients
of $-0.12$, $-0.45$, and $-0.07$, respectively). The Al concentration of the same extract was more strongly correlated with yield, giving partial regression coefficients of $-0.87$ for barley, $-0.45$ for rape, and $-0.61$ for alfalfa. As Al toxicity is likely to be encountered in many acid soils with Mn toxicity problems, accurate prediction of plant growth limitations is likely to require the determination of both elements. As a general rule, Mn toxicity alone may be encountered between pH 5.5 and 5.0, and both Mn and Al toxicity may be encountered below pH 5.0.

### 3.4 Manganese Determination

Manganese is readily determined at trace levels by a range of analytical techniques. Flame atomic absorption spectrometry (AAS) can determine Mn at concentrations in the range 0.1 to 10 mg L$^{-1}$, with an instrument detection limit of 0.01 mg L$^{-1}$ [49]. Interferences in the determination can be overcome using a combination of boric acid and strontium chloride (500 mg L$^{-1}$ each) [50]. Sensitivity can be improved by a liquid–liquid preconcentration extraction into a solution of 8-hydroxyquinoline in chloroform [51], by on-line preconcentration and solvent elution of diethyldithiocarbamate Mn complexes [52], or by adsorption of the Mn complexes with cupferron on activated carbon. The detection limit of the latter method is 1.8 µg L$^{-1}$ [53]. Greater sensitivity can be achieved using electrothermal excitation [54], with transverse heating and longitudinal Zeeman effect background correction systems achieving a detection limit of 0.026 µg L$^{-1}$ [55].

The simultaneous, multielement capabilities of inductively coupled plasma atomic emission spectroscopy (ICP-AES) have been widely exploited in the analysis of biological materials. The approach has a detection limit of 2 µg L$^{-1}$ for Mn [49] and has been used with preconcentration to improve sensitivity [52].

A range of colorimetric methods is used for the determination of Mn in waters. The most commonly used approach is based on the oxidation of Mn(II) by persulfate in the presence of silver nitrate to form the permanganate anion [49]. Flow analysis using this approach produced a linear response from 2.5 to 40 mg L$^{-1}$ Mn(II) and a detection limit of 1.2 mg L$^{-1}$ (99.7% confidence level) [56]. Recently developed chromogens are capable of measuring Mn(II) at much lower concentrations. The chromogenic system TCMOPPH2-Cd(II)-imidazole, using the novel synthetic chromogenic reagent meso-tetra[4-(carboxymethylenoxy)-phenyl]porphyrin (TCMOPPH2), achieved a linear range from 0.01 to 1.75 mg L$^{-1}$ with a detection limit of 2.8 µg L$^{-1}$ [57], and oxidation of Mn(II) in a strong basic medium and colorimetric determination using 3,3',5,5'-tetramethylbenzidine yielded a detection limit of 3 µg L$^{-1}$ [58].

Sensitive spectrophotometric determination of Mn(II) can be achieved by exploiting its catalytic effect on reactions. The catalytic effect of Mn(II) on the oxidation of diphenylcarbazone (DFC) in the presence of triethanolamine (TEA) has been employed for plant digests, achieving reproducible results in the concentra-
tion range 0.10 to 0.80 mg L\(^{-1}\) and a detection limit of 0.03 mg L\(^{-1}\) [59]. More sensitive procedures based on Mn(II) catalytic effects have been developed. A procedure based on the oxidation of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) with periodate permits measurement of Mn in the concentration range 0.05 to 1.0 µg L\(^{-1}\) and produced a relative standard deviation (RSD) \((n = 10)\) of 1.6% at 0.5 µg L\(^{-1}\) [60]. Other Mn(II) catalytic approaches include a reduced phenolphthalein-periodate reaction (linear range 2–200 µg L\(^{-1}\), detection limit 0.9 µg L\(^{-1}\)) [61] and decomposition of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (NANA) with hydrogen peroxide (range 0.2 to 1 µg L\(^{-1}\), detection limit 0.06 µg L\(^{-1}\)) [62].

4 ALUMINUM

4.1 Aluminum as a Plant Toxin

Although Al toxicity is recognized as the most common limitation to plant growth on acid soils, there are no identifiable symptoms of Al toxicity suitable for use as a diagnostic indicator [3], the most apparent effects being a reduction in both root and shoot growth. Typically, roots are more affected by Al toxicity than shoots. In plants exposed to high Al levels, elongation of the main axis is inhibited, and roots become thickened, stubby, brown, brittle, and occasionally necrotic [3].

Wood et al. [63] reported a critical Al\(^{3+}\) concentration for root elongation in white clover (Trifolium repens L.) of 30 µM, and the critical concentration for root hair formation was 10 µM. Hecht-Buchholz et al. [64] showed a limitation of root hair formation at a summed activity of Al monomers of 2.5 µM, and 12 µM completely inhibited root hair formation. Thus, microscopic effects on plant growth may occur at Al levels that do not affect the macroscopic appearance of the plant.

4.2 Solution Chemistry of Al

The chemistry of Al in aqueous systems is complex (even when relatively simple systems are considered) and has been the subject of considerable research (see reviews by Ritchie [10] and Sposito [65]). Aluminum entering solution coordinates with six water molecules that undergo hydrolysis to an extent determined by the solution pH (Table 1) [28]. Hydrolysis reactions are important at pH >4.0; >80% of the total Al is hydrolyzed at pH 4.9. As the extent of hydrolysis increases, the charge density of the Al molecule decreases and polymerization of Al units can occur. A diverse range of polymeric Al forms has been proposed, but the mechanism of their formation is not well understood. The amount and type of polymer formed may be influenced by the pH and Al concentration of the initial solution, the rate and extent of neutralization, the mixing conditions, and the time of aging [66]. Bertsch and Parker [66] considered that, of all the polymeric Al forms pro-
posed, those having the most convincing experimental support were \( \text{Al}_2(\text{OH})_3^{2+} \), \( \text{Al}_6(\text{OH})_{20}(\text{H}_2\text{O})_6^{4+} \), the "gibbsite fragment" model forms, \( \text{Al}_8(\text{OH})_{20}(\text{H}_2\text{O})_4^{4+} \), through \( \text{Al}_{54}(\text{OH})_{144}(\text{H}_2\text{O})_{36}^{18+} \), and the \( \text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+} \) species. It is generally accepted that polymeric Al forms are metastable intermediates in the precipitation of \( \text{Al(OH)}_3 \) and that a partially neutralized Al solution at equilibrium will contain only monomeric species and the stable solid phase [67]. Although polymeric Al forms may persist in pure solutions, they are unlikely to be important in soil solution given their high charge [66] and therefore high affinity for negatively charged soil surfaces. Brown and Hem [68] equilibrated synthetic Al solutions with various types of mineral surfaces and found that particulates rapidly facilitate the removal of polymeric Al. These solutions quickly reached an apparent equilibrium with respect to amorphous \( \text{Al(OH)}_3 \). In soil systems, the removal of polymeric Al forms would be further enhanced by the presence of flocculation-causing anions, such as phosphate, silicate, and sulfate [67].

In soil solution, complexation of Al by the inorganic anions \( \text{SO}_4^{2-} \), \( \text{F}^- \), and \( \text{NO}_3^- \) (Table 1) as well as by organic anions may occur. The activity of the \( \text{AlSO}_4^{+} \) ion pair will exceed the activity of the \( \text{Al}^{3+} \) species only where free \( \text{SO}_4^{2-} \) activity

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Equilibrium Reactions of Al Complexes at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Equilibrium reaction</strong></td>
<td>( \log K^{\text{a}} )</td>
</tr>
<tr>
<td><strong>Hydrolysis</strong></td>
<td></td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{H}_2\text{O} = \text{AlOH}^{2+} + \text{H}^+ )</td>
<td>-5.00</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al(OH)}_2^+ + 2\text{H}^+ )</td>
<td>10.1</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al(OH)}_3^+ + 3\text{H}^+ )</td>
<td>16.8</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al(OH)}_4^- + 4\text{H}^+ )</td>
<td>22.99</td>
</tr>
<tr>
<td><strong>Other complexes</strong></td>
<td></td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{F}^- = \text{AlF}^{2+} )</td>
<td>7.0</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 2\text{F}^- = \text{AlF}_2^+ )</td>
<td>12.7</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3\text{F}^- = \text{AlF}_3^- )</td>
<td>16.8</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 4\text{F}^- = \text{AlF}_4^- )</td>
<td>19.4</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 5\text{F}^- = \text{AlF}_5^- )</td>
<td>20.6</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 6\text{F}^- = \text{AlF}_6^- )</td>
<td>20.6</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{SO}_4^{2-} = \text{AlSO}_4^+ )</td>
<td>3.5</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 2\text{SO}_4^{2-} = \text{Al(SO}_4)_2^3^- )</td>
<td>5.0</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{H}_2\text{PO}_4^- = \text{AlH}_2\text{PO}_4^+ )</td>
<td>( \approx 3 )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{HPO}_4^{2-} = \text{AlHPO}_4^+ )</td>
<td>( \approx 7 )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3\text{NO}_3^- = \text{Al(NO}_3)_3^5^- )</td>
<td>0.12(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Formation constants are the selected values of Nordstrom and May [69].

\(^b\) Formation constant from Lindsay and Walthall [70].
exceeds $10^{-3.2}$ M (0.63 mM), and $\text{SO}_4^{2-}$ activities of $10^{-1}$ M (100 mM) would be necessary for the other Al-$\text{SO}_4$ ion pairs to become dominant [28]. Whereas $\text{SO}_4^{2-}$ activities in excess of $10^{-3.2}$ M are unlikely to be encountered in virgin, highly weathered soils, they may be present following fertilization [71]. Similarly, $\text{F}^-$ complexation of Al in virgin soils is likely to be low because soil solution $\text{F}^-$ concentrations are usually $\leq 10^{-5}$ M [72,73]; however, Al-$\text{F}$ pairs may be important where solution $\text{F}^-$ levels are elevated in fertilized soils through the application of $\text{F}^-$ present as an impurity in superphosphate [74]. Aluminum-$\text{SO}_4$ ion pairs will be of limited importance in soil solution as the affinity of Al for $\text{NO}_3$ is low [28].

Aluminum complexes formed with phosphate and silicate may also be important. Several authors have presented evidence for Al-OH-$\text{PO}_4$ polymers in dilute nutrient solutions at pH values from 4.1 to 4.8 [75–77]. Such forms were precipitated at higher pH values or increased concentrations. Silicate has been implicated in the solubilization of Al [78] and movement of Al through soil horizons [79].

In soil solution and natural waters, significant proportions of the soluble Al are present as complexes with organic ligands [80]. Aluminum complexation occurs predominantly with organic functional groups containing oxygen (COOH; phenolic-, enolic-, and aliphatic-OH groups; and possibly ketonic CBO and ester functional groups), whereas those containing nitrogen (amino acids and porphyrins) generally form weak complexes [81]. The relative importance of organic complexation in solution depends on the nature and concentration of the organic ligands, pH, ionic strength, and the kind and amount of competing cations. In a study of the stability of metal ion complexes with humic and fulvic acids, Schnitzer [82] found Al to be the second most stable complex; Fe complexes were more stable. A number of methods have been proposed to distinguish inorganic monomeric Al from organically complexed Al and polymeric Al forms. These are considered in the final section of this chapter.

### 4.3 Identification of Al-Toxic Soils

Measurements of the solid-phase characteristics of soils, such as pH, exchangeable Al, and Al saturation, have been widely used as diagnostic tools for the prediction of Al toxicity. Although critical values for such measures derived for a given crop on a given soil have generally provided a good prediction of plant performance, these predictors have not proved particularly useful when applied to a given species over a range of soils. Bell and Edwards [83] considered that the best relationships between plant growth and indices of Al availability would be found using soil solution parameters. Whereas studies in nutrient solution culture have shown that plant performance can be best predicted on the basis of the activity of monomeric Al in solution, attempts to relate plant performance to soil solution Al parameters have generally been unsuccessful. This may in part reflect our inabil-
ity to measure accurately the phytotoxic forms of Al present in soil solution. The following sections consider the various soil Al measurements used to assess soil acidity and their relative merits.

### 4.3.1 Solid-Phase Al

Exchangeable Al is the major reserve of labile Al and can readily enter the soil solution through exchange with other cations. The size of this reservoir is dependent on the cation exchange capacity (CEC) and the degree of Al saturation. For a given CEC, the amount of exchangeable Al is strongly pH dependent, decreasing with increasing pH to low levels at pH 5.5. Exchangeable Al is normally defined as the amount of the element extracted by an unbuffered neutral salt solution; 1 M KCl is most commonly employed, with the use of other salts producing slightly different results [84]. Whether this extracted Al is truly exchangeable is the subject of considerable debate. Aluminum extracted by 1 M KCl could include Al from precipitated or amorphous Al(OH)$_3$ [85] and disordered aluminosilicates, hydroxy-Al interlayers, or organic Al complexes [86]. Several authors have reported that Al activity in KCl extracts approached that supported by gibbsite dissolution [85,87], the cumulative amount of Al extracted being greater for concentrated extractants even after exhaustive leaching [88]. In response to the difficulties presented by neutral salt extraction, Kotze et al. [89] attempted to determine exchangeable Al by isotopic exchange with $^{28}$Al. They found that, in some soils, isotopically exchangeable Al did not appear to be related to neutral salt exchangeable Al and concluded that isotopic exchange provided an improved means of studying exchange reactions of Al. However, the validity of this approach is questionable because exchange of $^{28}$Al with Al atoms present as an integral part of soil minerals cannot be precluded.

Wada [90] proposed that, in ando soils where the soil pH is lower than the point of zero net charge, high-ionic-strength extractants caused adsorption of H$^+$ by variable charge surfaces resulting in an increase in extractant pH. This pH increase would result in precipitation of Al released from exchange sites on the soil, thus giving the impression of low exchangeable Al levels in such soils. In contrast, Gillman and Sumpter [91] concluded that for a range of highly weathered soils from north Queensland, Al extracted by 1 M KCl was exchangeable after finding that the extracted Al correlated well with the difference between measured CEC and the sum of exchangeable bases.

Exchangeable Al has been used as a criterion for the determination of lime requirement [92,93]. Such lime rate determinations require the application of an empirical factor to allow for the neutralization of acidity other than KCl-exchangeable Al; these multiplication factors vary widely, e.g., from the addition of Ca at 1.5 times the exchangeable Al level [92] to 6.5 times the exchangeable Al [94]. Numerous authors have employed salts other than KCl in an attempt to improve the prediction of lime requirement. The use of CuCl$_2$ has been advocated,
as the high affinity of Cu for organic sites will result in the release of organically complexed Al [95]. It is also considered to extract reactive interlayer Al [96]. Lime rates based on CuCl₂-extractable Al have been found to be excessive [97], as organically complexed Al does not contribute to titratable acidity [98]. The use of LaCl₃ has also been suggested, as its ability to extract Al is intermediate between those of KCl and CuCl₂ [99].

The degree of Al saturation of the CEC has been found to be a more successful predictor of Al toxicity than exchangeable Al [100]. For a given species on one soil or a group of similar soils, the increases in crop growth with increments of lime addition correlate well with reductions in Al saturation, but critical levels obtained from such studies are not quantitatively applicable to other soils [101]. Adams [102] and Kamprath [100] cite studies in which critical Al saturation values range from 5 to 25% for soybean growth, depending on the soil type studied. Similarly, Bruce [103] cites critical Al saturation values for corn ranging from 5 to 70% depending on soil type. Thus, Al saturation represents a poor predictor of Al toxicity over a range of soils.

In addition to representing a pool of reserve acidity, exchangeable Al occupies exchange sites that would otherwise be available to retain nutrient cations. This effect is accentuated by the reduction of the CEC of variable charge surfaces as pH decreases. Menzies and Gillman [104] considered that this loss of base cation retention capacity represents another facet of degradation resulting from soil acidification and proposed a degradation index (DI) capable of representing this form of soil quality deterioration.

\[
\text{DI} \% = \left( \frac{\text{CEC}_b}{\text{CEC}_{5.5}} \right) \times 100
\]

In this equation, CECₜ is the capacity of the soil to retain base cations at its field pH and CEC₅.₅ the CEC at a pH of 5.5 as measured by the charge fingerprint method [105]. Use of CEC₅.₅ was intended to provide an assessment of the soil’s condition prior to acidification; the exchange is essentially free of Al, and the surface charge density increased by the increased pH. If the pH of the system prior to acidification were known, this pH could be used in place of pH 5.5.

Extraction with 0.01 M CaCl₂ has been used to assess the potential for Al toxicity [39]. In contrast to the extraction of the total exchangeable Al pool by concentrated extractants (a capacity measurement), the use of 0.01 M CaCl₂ is intended to provide an indication of the Al concentration present in the soil solution (an intensity measure). This approach has been used in Australia with considerable success over a range of soil types and for numerous plant species [106].

### 4.3.2 Soil Solution Al

Adams and Lund [107], in a series of experiments investigating the effects of Al toxicity on cotton root elongation, found that reasonable prediction of Al toxicity
could be achieved if soil solution Al concentration were corrected to molar activities. They reported a critical Al activity (90% relative root length) of 1.5 \( \mu \text{M} \) for cotton in three subsoils. Their calculations assumed that all Al was present as \( \text{Al}^{3+} \). Adams et al. [108] showed reduced root penetration into subsoils by cotton at <1 \( \mu \text{M} \) Al, and Adams and Pearson [109] found reduced peanut (Arachis hypogaea L.) root growth in subsoils at 9 \( \mu \text{M} \) \( \text{Al}^{3+} \) activity. Similarly, Richburg and Adams [110] found reduced penetration of cotton roots into three surface soils at 10 to 17 \( \mu \text{M} \) Al activity. Following calculations to account for hydrolysis reactions, critical Al activities of <2 \( \mu \text{M} \) were determined.

In contrast to the success of these early experiments, subsequent studies using the same approach have been less satisfactory [101,111]. Adams and Moore [112] and Adams and Hathcock [101] noted ambiguities in the relationship between plant growth and the Al level measured. Aluminum toxicity appeared in some soils with Al concentrations ranging from <0.4 to 14 \( \mu \text{M} \), and the range for nontoxic horizons was <0.4 to 134 \( \mu \text{M} \). Ranges of summed activities of \( \text{Al}^{3+} \), \( \text{AlOH}^{2+} \), and \( \text{Al(OH)}_{2}^{+} \) were <0.3 to 10 \( \mu \text{M} \) and <0.3 to 98 \( \mu \text{M} \) for toxic and nontoxic horizons, respectively.

The inferiority of relationship between Al activity and plant growth derived from soil culture experiments, relative to those derived in carefully controlled solution culture studies, has generally been attributed to the inability of analytical procedures to discriminate inorganic monomeric Al forms from organically complexed Al [101,112,113]. An additional factor may be the influence of matrix effects in soil culture studies. Horst et al. [114] found that, in order to inhibit sorghum root growth to the same degree, a 10 times higher Al level was required in sand culture than in solution culture. They suggested that this discrepancy may be due to (1) slower movement of Al to the roots by diffusion in sand than by convection in aerated solution culture, (2) increased pH at the root surface leading to precipitation of Al, and (3) enhanced release of root exudates that complex Al. Although the experiment of Horst et al. [114] considers matrix effects that may occur in soil, Al supply is limited by mass flow of solution, or diffusion of Al, and the total concentration of Al in solution is fixed. In soil culture, additional Al can be released into solution by mineral dissolution or cation exchange. Furthermore, as these effects can take place in the immediate vicinity of the root, the plant’s capacity to detoxify Al may be quickly overcome. Nevertheless, as matrix effects may be important, care should be taken in the comparison of critical values derived from solution and soil culture experiments.

Studies conducted in solution culture under carefully controlled conditions have demonstrated that the activity of Al in solution is a more accurate predictor of Al toxicity than Al concentration [111,115]; however, the relative toxicity of the individual ionic species remains unclear. A particular difficulty is presented by the monomeric hydrolysis species because several of these species coexist in solution; thus, individual species cannot be investigated in isolation. Furthermore,
the activities of individual species must be calculated from equilibrium data that may be uncertain [116]. It appears that Al^{3+} is toxic and the Al-OH pairs are less toxic or nontoxic [117].

Phytotoxicity of polynuclear Al has been demonstrated in culture solutions of simple chemical composition [118,119], with Parker et al. [120] identifying Al_{13} as the specific ion responsible. Toxicity of this species toward wheat is some 5 to 10 times greater than that of Al^{3+} when compared as concentrations of atomic Al in each form (a comparison based on moles of each molecular species would result in an even larger differential toxicity), with \approx 3 \mu M Al as Al_{13} producing complete inhibition of root growth. Although conditions suitable for the formation of Al_{13} may occur in simple culture solutions, these polymers are unlikely to be encountered in soil systems.

Results of studies conducted in nutrient solution culture have indicated that Al ion pairs with SO_{4}^{2-} [121,122] and F^{-} [122,123] are nontoxic or less toxic than Al^{3+} or Al ion pairs with OH^{-}. The nontoxicity of AlSO_{4}^{3-} has also been indicated by soil culture experiments [9,113,124]. Ion pairs of Al with F appear to be toxic, although less so than Al^{3+}. Kinraide [117] concluded that the relative toxicity of Al ions to wheat roots was Al_{13} > Al^{3+} > AlF_{2}^{+} > AlF^{2+}.

The nontoxicity of organically complexed Al has been suggested by nutrient solution culture studies in which the toxicity of Al was ameliorated by the addition of organic acids [118,125,126]. This conclusion has also been inferred from the observation that addition of organic matter to acid soils results in amelioration of Al toxicity [127]. However, more careful investigation of this amelioration has revealed that pH changes resulting from organic matter addition may be more important than complexation of Al [127,128]. The soil pH change that will result from an organic matter addition can be predicted from the basic cation content of the material [129].

Aluminum toxicity rarely occurs above pH 5.0. As the pH decreases below this value, the solubility of Al-containing minerals increases exponentially; thus, the probability of Al toxicity to plants becomes higher as pH decreases [70]. There appears to be no unique relationship between soil pH and solution Al [110], and pH has not proved to be a good indicator of Al toxicity [107]. Nevertheless, pH can be an effective predictor of Al toxicity across soils of similar mineralogy. In highly weathered soils, soil solution pH was an effective predictor of Al toxicity as assessed by root elongation [9,113,128]. In these soils, pH is an effective predictor of root growth inhibition because of its strong correlation with Al^{3+} activity; this relationship is attributed to the control of Al^{3+} activity by gibbsite dissolution [73,130]. Measurements of soil solution pH also account for root growth limitations attributable to H^{+} ion toxicity.

Numerous studies have indicated that increasing concentrations of Ca can mitigate the adverse effects of Al on plant growth. This amelioration appears to result from the displacement of cell-surface Al by Ca-induced reduction in cell
surface negativity and to a lesser extent from the restoration of the cell surface to nonlimiting levels of Ca [131]. To accommodate specific ameliorative effects of Ca on Al toxicity, various Ca-Al activity ratios have been proposed as diagnostic indices of Al toxicity for crop and pasture species [111,132,133]. Ratios of soil solution Al to Ca have also been employed to assess the impact of soil acidity on deciduous and coniferous forests. Cronan and Grigal [134] concluded in their review of this research that “there is a 50:50 risk of adverse impacts on tree growth or nutrition when the soil solution Ca/Al ratio is as low as 1.0.”

4.4 Aluminum Determination

Aluminum is generally present in solution in soils and natural waters at low concentrations [71,135]. Thus, with the exception of very acidic waters, analytical methods with detection limits of 0.5 \( \mu \text{M} \) or less are often needed [136]. This issue is accentuated in chromatographic methods requiring postcolumn Al quantification. The numerous forms of Al that may be present further complicate the situation. To identify accurately soils that present plants with an Al challenge, the analytical approach used must be able to discriminate between toxic and nontoxic forms of Al. This section considers methods used for the determination of total Al, with particular emphasis placed on errors caused by the presence of dissolved organic matter or particulate Al and on the determination of specific forms of Al in solution (speciation).

4.4.1 Atomic Absorption and Emission Spectroscopy

Flame atomic absorption spectroscopy (flame AAS) has limited sensitivity for Al even with the use of the \( \text{N}_2\text{O}/\text{C}_2\text{H}_2 \) flame (optimum range 5 to 100 mg L\(^{-1}\)), due to the formation of refractory oxides [49]. Although the low sensitivity of this technique prevents its direct use on natural water samples, effective measurement of Al has been achieved with flame AAS using a prior extraction and concentration into a nonaqueous solvent. Hsu and Pipes [137] extracted the Al–8-hydroxyquinoline complex from 1000 mL of sample into 5 mL of benzene. A sensitivity increase of greater than 100-fold was achieved, but the large volume of sample required makes this approach impractical in soil solution studies.

Sensitivity of AAS for Al can be greatly improved through the use of graphite tube atomizers; detection limits of around 0.005 \( \mu \text{M} \) have been achieved using this method [138]. The sensitivity of the method is dependent on the nature and age of the graphite tube employed [139] and the nature of the sample matrix [140]. Several researchers have reported that AAS determination of Al using a graphite tube atomizer includes the majority of Al in particulate forms. Carrondo et al. [141] reported Al recoveries of 95–100% for type A zeolite, and Playle et al. [142] reported recoveries of 81–93% for kaolinite; particle size distribution in the sample was not reported in these studies.
A detection limit of \( \approx 10 \, \mu g \, L^{-1} \) can be achieved for Al by ICP-AES using the 396.15 and 308.21 nm lines [143]. Further improvements in sensitivity of ICP-AES for Al can be achieved using a sensitive line at 167 nm in the vacuum ultraviolet range [144]. Preconcentration using Chromazurol S immobilized on a silica gel achieved an enrichment factor of 50 [145]. As very high temperatures are produced in the plasma, it is anticipated that all forms of Al in the sample will be measured. Ambe and Nishikawa [146] found a recovery efficiency of \( >80\% \) for Fe and Al in particles 0.4 to 1 \( \mu m \) in diameter. Lower recoveries were found for larger particles, which may be due to the behavior of these heavier particles during the aspiration phase rather than failure to atomize within the plasma.

4.4.2 Spectrophotometric Methods

Colorimetric methods for Al determination have been in use for many years and, despite the upsurge in popularity of spectroscopy, they are still widely used [136]. Colorimetric methods offer the advantages of low cost and equipment requirements, ease of use, and good sensitivity. A range of colorimetric reagents are available for the measurement of Al, although some are unsuitable for natural waters because of their low sensitivity or interference by commonly encountered ions [147]. Only the more sensitive and commonly used methods are considered here.

Aluminon was one of the earliest reagents used for the determination of trace amounts of Al [148]; however, the method offers only moderate sensitivity, as the absorptivity of the complex is \( \approx 2 \times 10^4 \, L \, mol^{-1} \, cm^{-1} \) [149], and most techniques require a heating step [150]. Jones and Thurman [151] developed a method for Al determination based on Eriochrome cyanine R (ECR). This reagent offers high sensitivity for Al with a molar absorptivity of \( 6.75 \times 10^4 \, L \, mol^{-1} \, cm^{-1} \) [147]. Potential interferences from F, PO\(_4\), and Fe may be a problem in natural waters.

Aluminum determination through the formation of the Al–8-hydroxyquinoline complex followed by solvent extraction of the complex and spectrophotometric measurement [152] is the most sensitive of the commonly used spectrophotometric methods [136]. Although the solvent extraction procedure adds an additional step to the method, the Al complex formed is stable in the organic phase; Bloom et al. [153] reported no change in absorbance after storage of the extract at ambient temperature for 24 hours. Polymeric Al and particulate Al have been reported to be excluded when extraction is performed at either pH 5.0 [153–155] or pH 8.3 [155]. Although this method offers good sensitivity and discrimination against particulate forms of Al, its applicability to soil solution studies is limited by the large volume of sample required (25 to 100 mL [153,155]).

Dougan and Wilson [149] compared the performance of aluminon, ECR, and a number of other reagents, including pyrocatechol violet (PCV), which had received little prior evaluation for Al determination. They found the PCV method
to be sensitive for Al, with a molar absorptivity of $6.3 \times 10^4$ L mol$^{-1}$ cm$^{-1}$, and to be relatively free of interferences. Iron interference can be eliminated by reduction to the ferrous form and complexation with 1,10-phenanthroline. The simplicity of the PCV method of Dougan and Wilson [149] makes it well suited to automation [156]. Automation has been reported to offer increased precision, coefficients of variation being 6.8% for the manual method of Dougan and Wilson [149] and 2.9% for an automated approach [157]. A potential problem in automated methods is due to their speed of analysis. In automated methods, the sample is acidified to cause decomplexation of Al from organic ligands as a component part of the analysis; thus, the period of acidification prior to analysis is reduced to as little as 1 minute. As the kinetics of Al-fulvate interaction are relatively slow [158], it is unlikely that such a short period of acidification would result in effective decomplexation of Al from organic ligands. Røgeberg and Henriksen [159] found little beneficial effect from addition of acid in an automated method and discarded acid addition in their final method.

Røysset and Sullivan [156] reported that natural organic ligands could compete with added complexing agents for Al, causing negative interference in the determination of Al. In a comparison of Al determination by PCV, ECR, and 8-hydroxyquinoline (pH 8.3) with extraction into methyl isobutyl ketone, Røysset and Sullivan [156] found that the 8-hydroxyquinoline method was not affected by the presence of humic and fulvic acids at 10 to 200 mg L$^{-1}$ organic C. The presence of organic ligands did interfere with ECR at organic C concentrations greater than 50 mg L$^{-1}$ and with PCV at organic C concentrations greater than 10 mg L$^{-1}$. However, this result is probably attributable to the short reaction time in the automated analytical method used. Dougan and Wilson [149] reported that the presence of humic and fulvic acids caused only a very small reduction in the Al concentration determined by PCV in acidified samples. Determination of Al without prior acidification resulted in underestimation by 5 to 10% and 30 to 50% in solutions containing organic C concentrations of 10 mg L$^{-1}$ and 200 mg L$^{-1}$, respectively [156].

The interference caused by organic ligands in the determination of Al can be overcome by destruction of these ligands by photo-oxidation. The use of photo-oxidation of freshwater samples as a step in trace metal speciation schemes was pioneered by Florence [160], who reported that measurements of total Cd, Cu, Pb, and Zn before and after ultraviolet (UV) treatment showed no losses. In contrast, Laxen and Harrison [161] reported that irradiation of a number of river water samples resulted in a considerable increase in pH and loss of labile metals as measured by anodic stripping voltammetry. Campbell et al. [162] reported losses of $\approx 20\%$ of the total Al content during photo-oxidation despite little change occurring in the solution pH during photo-oxidation. They attributed this loss to adsorption of Al by the quartz tubes used. Bloom and Erich [136] proposed that the Al losses
observed by Campbell et al. [162] were due to precipitation of Al(OH)_3 during heating of the samples; the solubility of Al(OH)_3 decreasing with increased temperature. Bloom and Erich [136] concluded that heating should be avoided during photo-oxidation or acid should be added to prevent precipitation.

Extremely sensitive determination of Al is possible using fluorimetric methods [147]. The most commonly employed reagent, lumogallion [3-(2,4 dihydroxyphenylazo)-2-hydroxy-5-chlorobenzene sulfonic acid], is reported to have a detection limit of 0.05 µg L\(^{-1}\) [163], although this can be improved to 0.02 µg L\(^{-1}\) by the addition of the nonionic detergent Triton® X-100 [164] or to 0.007 µg L\(^{-1}\) by extraction into n-hexanol [165]. A method based on the formation of a 1:1 complex with chromotropic acid (1,8-dihydroxynaphthlene-3,6-disulfonic acid) in a methanol medium provides a linear response in the concentration range 2 to 100 µg L\(^{-1}\), with a detection limit of 1.0 µg L\(^{-1}\), and has been used successfully on tap, river, and seawater samples [166]. Fluorescence by dissolved organic matter and competition for Al by natural organic ligands may cause interference in fluorescence methods [163]. Further problems may arise through the high sensitivity of these methods accentuating the problems posed by Al contamination. Use of double distilled water is recommended, but storage should not be in glass [163]. Care should be taken to avoid containers that may contain fluorophoric compounds able to leach into solutions [136].

4.4.3 Speciation of Al

Aluminum may be present in solution in a variety of forms including Al\(^{3+}\), inorganic ion pairs, organically complexed Al, and polymeric forms. Studies of the effects of Al on plant growth have indicated that these forms have different toxicities. Thus, it is often necessary to determine the speciation of Al in solution rather than the total concentration present. The activity of Al species in solution may be calculated from thermodynamic principles, and several computer speciation programs have been written to perform these calculations [167,168]. Although this approach has been successful in simple well-defined systems, it has proved less satisfactory in systems containing organic ligands. Hue et al. [125] used a computer-based mathematical model to calculate monomeric Al activity in the presence of short-chain carboxylic acids. Organic acid concentrations were determined by high-performance liquid chromatography, and the Al concentration was measured by ICP-AES. Poor agreement between calculated monomeric Al activity and root growth, relative to inorganic Al controls, was attributed to imprecise association constants and the failure of the analytical methodology to identify and measure all organic ligands. Thus, speciation of Al in natural waters by thermodynamic calculations, is, at present, precluded by analytical difficulties [125] and the lack of reliable association constants [69].

An alternative approach to the problem of speciation of Al in complex natural water systems has been the use of analytical methods that aim to measure spe-
cific forms of Al. These techniques include short-term reactions with complexing agents [153–155,169], dialysis [170,171], cation exchange resins [162,172], F\(^{-}\) ion-selective electrometry [80,172], ion chromatography [173,174], and the use of selective reagents [175,176]. This section briefly considers the applicability of a number of these approaches to soil solution studies, with particular emphasis placed on characteristics of the methods that restrict their use. A detailed review of Al speciation methods is given by Bloom and Erich [136].

The ion exchange column procedure [172] has been widely used for the speciation of Al in environmental samples [136]. Ion exchange attempts to separate inorganic and organically complexed Al by passing samples through an ion exchange resin that retains free hydrated metals and labile complexes. Inaccurate results may arise as a result of sample pH change occurring during passage of the sample through the exchange column and through disruption of the equilibria between the various Al forms [177]. Changes in pH can be minimized by matching column pH and cation composition to those of the sample [162]. Whereas preparation of columns compatible with sample composition may be appropriate in studies involving repeated samplings of river and lake waters, this approach is made impractical in soil solution studies by the diversity of solution compositions encountered. A more widely applicable approach presented by Powell [178] uses a solution–exchanger contact time of around 1 second to minimize disruption of sample equilibria.

Ion chromatography has received considerable interest as a means of separating Al forms [173,174,179]. The approach is capable of separating F\(^{-}\), oxalato-, and citrato-aluminum pairs [173,174]. However, phytotoxic Al\(^{3+}\) and nontoxic Al-SO\(_4\) ion pairs were eluted together, the outer sphere Al-SO\(_4\) complexes dissociating in the presence of the sulfonate exchange sites of the column resin [173]. The use of ion chromatography for the speciation of soil solutions may also be limited by the potential for redistribution of species due to differences in sample and eluent ionic strength and pH [173] and the adsorption of humic acids by the exchange resin [174].

Equilibrium dialysis has been used for the speciation of Al [170,171]; however, its use is restricted by the large volume of solution required and the length of time taken to reach equilibrium (≈48 hours) [171]. Furthermore, the effectiveness of this approach may be limited by the potential for permeation of low-molecular-weight organic molecules through the membrane [170,180,181].

Several methods have been proposed that employ selective chelating agents to determine inorganic monomeric Al. Evans and Zelazny [175] proposed a method that utilizes the decrease in absorbance of crown ether at 273 nm due to chelation with Al\(^{3+}\). Because no phase separation of the organic solvent containing the crown ether occurs in the proposed method, the humic and fulvic acids present in soil solution contribute a high background absorbance at 273 nm [177]. Morin has also been proposed as a reagent specific to inorganic monomeric Al
forms [176]; however, as Ca$^{2+}$ and Mg$^{2+}$ contribute interferences, this method is unlikely to prove effective in soil solution studies.

Short-term colorimetric methods are easy to use and require a small volume of sample. In general, these methods assume that only inorganic monomeric Al forms react with the chromogen during the reaction period used. Kerven et al. [177] demonstrated that, for five short-term colorimetric methods, this assumption was invalid. The best discrimination was achieved by a 15-second 8-hydroxyquinoline method [154]; this method measured 46% of organically complexed Al as inorganic monomeric forms. The remaining methods, which involved longer reaction times, measured >80% of the organically complexed Al as inorganic monomeric forms. The method of Kerven et al. [169] assumes that both inorganic and organic forms of Al will immediately begin to react with an added chromogen but that their rates of reaction will vary. This method uses a series of calibrating solutions containing a known total Al concentration prepared with varying ratios of inorganic monomeric Al and organically complexed Al. Aluminum in unknown samples is fractionated into inorganic monomeric and organically complexed forms on the basis of a short-term reaction with PCV or aluminon and a total Al measurement by ICP-AES.

5 CONCLUSIONS

In many acid soils, Al presents the primary challenge to plant growth; thus, the chemistry and phytotoxicity of Al have been extensively researched and are reasonably well understood. However, the identification of Al-toxic soils remains fraught with difficulties. Although it is generally accepted that measurement of the activity of phytotoxic ionic species in soil solution provides the best correlation with plant response, the cost and labor-intensive nature of this approach preclude its adoption for routine soil testing. Simpler measures, such as 0.01 M CaCl$_2$-extractable Al or measurement of soil pH, are inexpensive and sufficiently effective as predictors of Al toxicity to provide an effective routine soil-testing tool.

Identification of Mn-toxic soils is an even greater challenge than identifying those that are Al toxic. This difficulty stems from the ephemeral and heterogeneous nature of reducing conditions in soil and from the potential for interactions of Mn with several other plant nutrients. Further difficulties arise as typical soil-handling procedures, such as air drying, alter the soil Mn status. The most effective approach may be to use 0.01 M CaCl$_2$-extractable Mn and to consider the soil pH.

REFERENCES


130. RC Bruce, LC Bell, DG Edwards, LA Warrell. Chemical attributes of some Queens-


Using Lime to Ameliorate Topsoil and Subsoil Acidity

Doug C. Edmeades  
agKnowledge, Ltd, Hamilton, New Zealand  
Anna M. Ridley  
Agriculture Victoria, Rutherglen, Australia

1 INTRODUCTION

This chapter considers the practice of liming—what information is required and hence what measurements should be made to answer the questions, is a soil acid, is lime required, and, if so, how much lime should be applied? These questions are approached from the practical perspective of an advisor in the field. Such questions go beyond the technical issues, and some discussion of the economic and indeed social and cultural issues related to liming is offered.

This chapter does not attempt to review comprehensively and condense the existing scientific literature. Rather, the approach is to attempt to put information consolidated in other reviews, including this book, into a practical context and framework.

The very concept of soil acidity and how it is measured has changed remarkably over the last 50 years as understanding has developed. The early concepts and definitions of optimal soil pH and lime requirement were based largely on what are now referred to as soils with permanent negative charge. It is now re-
alized, however, that most soils, especially acid soils, contain some variable negative charge. The “acidity” in such soils depends on the pH at which it is measured. This has, or at least should have, had a major effect on how soil acidity and lime requirements are measured and interpreted.

Such changes in response to new understanding are essential, but they can also give rise to confusion and, in the extreme, apparent conflicts in the scientific and advisory literature. This can be very difficult for “new” scientists, technicians, and advisors—those, it is suggested, at the “front line” in terms of making decisions about the need for lime. Furthermore, change required at the technical level can be resisted by cultural attitudes toward liming. These must also be challenged. For these reasons, the chapter begins by briefly tracing the origins and subsequent developments of some of the important concepts and measurements related to soil acidity, indicating where progress could be made to improve decisions about lime use.

For the purpose of this chapter, liming is defined as the application of ground calcium and/or magnesium carbonates, hydroxides, and oxides, although it is appreciated that the latter two types of products are seldom used in practical agriculture today.

2 SIGNIFICANT DEVELOPMENTS

2.1 Optimal pH

Historically, the “ideal” soil was thought to be one that contained no acidity. For some, this was initially taken to be pH 8.2 to 8.4 because this was the approximate pH of a soil in equilibrium with fine limestone. Others interpreted “no acidity” to mean that the cation exchange capacity (CEC) of the soil was 100% saturated with the basic cations (Ca, Mg, K, and Na). Because, by convention, CEC was measured at pH 7, this pH became the ideal [1,2]. No doubt this was reinforced by the simple chemical fact that at pH 7.0 the concentrations of acid (H⁺) and base (OH⁻) are equal.

With increasing field experience, it was soon realized that the optimal soil pH, i.e., the pH at which crop production was maximized, was not only different from the theoretical ideal but also different for different crops.

Russell [3] discussed the many problems in measuring and interpreting soil pH and concluded, “For general advisory purposes, there is no justification in measuring it to an accuracy of greater than 0.2 unit and probably to one greater than 0.5 unit.” He outlined the conundrum as “Crops differ in their susceptibilities to these consequences of acidity; hence it is impossible to draw up any table showing the critical pH at which a given crop begins to suffer severely from acidity, even if any definite meaning could be given to the pH figure.”

Russell also noted the discrepancy between laboratory- and field-determined lime requirements and the arbitrary choice of target pH inherent in defining lime
requirements, suggesting that “It [lime requirement] is a useful concept that can have no exact meaning.” Consequently, he advised a pragmatic solution to the liming problem, suggesting that “The correct amount is found by continual check on pH or crop performance whenever additional dressings of lime are given.”

Woodruff [4] was more precise. He stated, “the observation by Veitch (1902) that maximum crop yields were obtained by liming soils to less than pH 7 has been substantiated by numerous investigators.” He suggested that this discrepancy arose because plants need only pockets of neutralized zones for maximum production.

In discussing the optimal pH requirements for a range of crops, Woodruff [4] went further, stating that “The actual soil pH requirements of crops are not in close agreement with the pH recommendations that are offered by the various advisory services.” Reflecting perhaps a greater confidence in soil chemistry than agronomy, he stated, “Seldom are the results from field trials used to determine whether soils should be limed. Instead, chemical soil tests and other criteria are used to arrive at such decisions.”

Despite all these reservations, most early texts provided readers with tables showing the degree of tolerance of various crops to acidity together with discussion of the laboratory methods for measuring how much lime is required to achieve pH 7 or greater.

This inconsistency can still be found today and arises from the early theories on soil acidity and practical experience in the field. The pH requirement has to a large extent been resolved at the technical level due to our better understanding of soil chemistry, particularly the chemistry of variable charge soils; agronomy; and plant physiology.

It is now more clearly understood that much of the acidity measured when soils with variable charge are titrated to a pH of 7 or 8.2 is pH dependent and does not affect the growth of the plant at the in situ soil pH [2,5]. For example, beginning with Kamprath [6] and Reeve and Summer [7], it is now accepted that on many soils it is primarily the Al component of exchangeable acidity that affects plant growth and that liming to reduce this component of acidity is sufficient to optimize plant growth. The optimal pH on such soils is consequently much lower than the “ideal” of 7 or 8.2. However, this applies only to soils in which Al toxicity is the major factor limiting growth (see Sec. 2.5).

The importance of the Al component of exchangeable acidity is reinforced by independent evidence from solution culture studies showing that most crops are not sensitive to \( H^+ \) ion toxicity per se but that small (\( \mu \)M) concentrations of Al can dramatically decrease plant growth (see Refs. 8 and 9 for examples). It is also beyond doubt that crop species, and cultivars within species, exhibit differential tolerance to Al (see Sec. 3.2 and Chapter 15).

With these developments, it is entirely appropriate to include in the definition of optimal pH the notion of “fitness for purpose.” The ideal or optimal pH for
a given soil, in terms of crop production, must be defined in functional terms by including the crop and perhaps the cultivar to be grown.

2.2 Measuring Soil pH

Less progress has been made in modifying the techniques used to measure soil pH and trying to incorporate our recent understanding of acid variable charge soils.

It has been known for a long time that the soil pH—more correctly the pH of a solution in equilibrium with the soil—is affected by the strength of the electrolyte, among other things. Thus, temporal variations in soil pH were attributed to changes in soil moisture or recent additions of fertilizer [3]. The results in Fig. 1 are frequently used to demonstrate this relationship, often with the implication that soil pH is an unreliable measurement. It was for this reason that Schofield and Taylor [10] suggested that pH should be measured in 0.01 M CaCl₂ to eliminate these effects. This concentration was chosen because it was thought to represent the concentration of Ca in temperate soils. There is now clear evidence that the ionic strength (I) of soil solutions of field soils, including both temperate and tropical soils, is about 0.003 to 0.005 M [11–15].

There is also evidence that soil solution ionic strength varies in a predictable seasonal manner, being higher in the summer (low soil moisture) and lower in the
winter (high soil moisture). The pH of the soil solution and, to a lesser extent, the soil pH (if it is measured at a suitably low ionic strength) vary in a predictable inverse manner \[12,13,16\]. These effects can be large. For example, Edmeades et al. \[12\] measured seasonal extremes of 0.002 to 0.009 M in soil solution ionic strength and 6.0 to 6.5 in solution pH. The question arises, however, should the methods used for measuring soil pH, and indeed extractable Al and Mn, be modified to include these effects or eliminate them, as has been past practice?

It is reasonable to assume that plants respond to soil conditions through the medium of the soil solution. It is to be expected, therefore, that the pH and the concentrations and form of Al and Mn in the soil solution, at the prevailing field conditions, will have a significant impact on plant growth. There is some circumstantial evidence supporting this view, but further investigation is required.

Edmeades et al. \[17\] noted that pasture responses to lime are greatest in the summer–autumn seasons, corresponding to the time of highest ionic strengths and lowest pH. The implication is that Al toxicity is also expressed in a seasonal manner. They suggested, therefore, that it might be possible to improve the prediction of lime responses using methods that better reflected both the prevailing and constantly changing soil solution conditions.

More convincing, Carr et al. \[18\] accounted for 60% of the variation in wheat yields across a wide range of soils in Western Australia using subsoil Al, extracted at the soil solution concentration (0.005 M KCl). The ratio of Al to Na was superior to Al alone, suggesting that Na, an indirect measure of past fertilizer history, accounted for site-to-site differences. These results support \[15\] the suggestion of Slattery et al. that the form of Al extracted into solution at normal field ionic strengths might be quite different from the forms extracted into 0.01 M CaCl₂ \( (I = 0.03 \text{ M}) \) and 1 M KCl \( (I = 1 \text{ M}) \).

More studies, such as those by Dolling and Ritchie \[19\] and Edmeades et al. \[20\], are required to define the measurement conditions (soil/solution ratio, electrolyte type and strength) that best mimic the ionic strength prevailing in situ in the field. This work should be coupled with an examination of the concentration and speciation of Al and Mn.

### 2.3 Measuring Lime Requirements

There have been two reviews \[2,21\] of the many methods that have been developed to measure soil lime requirement—the amount of lime required to achieve a desired, and generally arbitrary, soil pH.

The basis for most of these methods, and in particular the choice of the desired pH, can be traced back to the early concepts of soil acidity—exchangeable acidity or base saturation \[2,5\]. As discussed earlier, these concepts are no longer appropriate, especially on variable charge soils. Other methods for measuring lime requirements that use or are calibrated against a laboratory-determined lime
requirement are equally flawed, given the discrepancy that exists between field- and laboratory-determined lime requirements [3,5].

For these and other reasons, both reviewers [2,21] expressed caution about the use of these methods. In particular, Black [2] made an important distinction between the soil lime requirement, the amount of lime to achieve an arbitrary desired pH, and the biological lime requirement (BLR), the lime required to eliminate restrictions to plant growth.

The best early example of this move toward defining the soil lime requirement in terms of the biological lime requirement for the plant comes from the work of Kamprath [6] and Reeve and Sumner [7], but others have also embraced the concept. In New Zealand, Edmeades et al. [22], having shown that the biological optimal pH for pasture is 5.8 to 6.0, used data from field trials to determine the amount of lime required to achieve pH 6.0—the field lime requirement, or to use Black’s concept, the biological lime requirement. Slattery and Coventry [23] adopted a similar approach in Australia for a range of crops and soils, defining the lime requirement as the amount of lime to obtain 90% of maximum yield.

Interestingly, the preceding studies suggest that it may be possible to determine the BLR from simple soil measurements that are routinely made. For a set of New Zealand soils, the field lime requirement was correlated with the initial soil pH and the organic matter content [24]. Bailey et al. [25] found similar results in the United Kingdom (UK). For some Australian soils [23], the initial soil pH, together with soil Al, was a useful predictor of field lime requirement.

Although these approaches are useful and accommodate our modern understanding of the soil–plant acidity complex, what is urgently required is field information defining the buffer capacity of soils—the unit change in soil pH per unit of acid or base applied. Such information, together with the initial pH and the optimal pH, could be used to determine the biological lime requirement for any given crop × soil combination (see Sect. 3.3.1). Furthermore, such information is essential for predicting the magnitude of soil pH changes that result from management-induced soil acidification.

2.4 The Acidification Process

It is now understood that soil acidification is not solely the result of the properties of the parent material and weathering but also occurs as a result of management practices. The major processes contributing to soil acidification under agricultural systems are now well understood as detailed by Helyar and Porter [26] and De Klein et al. [27] or more simply by Hollier [28].

The question of whether lime is required is no longer restricted to soils that are currently acid. Lime is also required on soils that are currently at their biological optimal pH to prevent them from become more acid. The thinking, and hence research, must go beyond the question of how much lime is required to achieve
the optimal pH and include the assessment of how much lime is required to maintain the optimal pH.

Several models of the soil acidification process in cropping and pastoral systems have been developed [26,27]. These are very useful tools, and it is now possible to calculate the amount of acidity or alkalinity produced by any pastoral or cropping system. Some typical estimates are given in Table 1. However, the technical limitation confronting the practical application of these acidification models is information on the buffer capacity of soils in the field required for converting the rates of acid produced into the amount of lime required to neutralize this acidity. The publications by Ridley and Coventry [32] and De Klein et al. [27] highlight this problem. Unfortunately, there is a paucity of data on this topic (Table 2). Why this should be so, when it is such a fundamentally important measurement in terms of making lime decisions, is difficult to understand, especially given the low cost involved in making such measurements.

What is remarkable is that the amounts of lime required to neutralize the acidity produced in cropping and pastoral systems, and hence maintain the soil pH, are not large on an annual basis, ranging from about 100 to 600 kg ha⁻¹ of limestone. From an economic perspective, problems arise because of the compounding nature of soil acidification over a long period of time, the remedy for which is large capital inputs of lime at rates of several tonnes per hectare. This frequently puts the cost of remedial action beyond the reach of the individual farmer. In this respect, the solution to the soil acidity problem facing many countries is similar to that of correcting P deficiency. The farmers may be able to pay for the ongoing maintenance inputs of P once the soil is productive, but the initial capital input to achieve this is beyond their resources.

An important consequence of the better understanding of the soil acidification process is that there is now a greater awareness of subsoil acidification as a factor limiting soil productivity. Even if the topsoil is sufficiently fertile, plant growth may be limited by subsoil acidity affecting its access to water and reducing its tolerance to drought [39,40]. Decisions about the need for lime must go beyond the “plow layer” and must take into account the subsoil.

2.5 Understanding the Specific Effects of Acidity on Plant Growth

Much progress has also been made unraveling the specific causes of poor plant growth in acid soils. This has provided further independent evidence that the old concept of the ideal pH soil is no longer tenable.

There is currently much emphasis on Al and Mn toxicity as factors limiting plant growth on acid soils. But this needs to be put into context. Although Al and Mn toxicity may be problems on many acid soils, nutrient deficiencies such as Ca, P, N, and Mo are also widespread. As increasing the soil pH by liming can in-
### TABLE 1  Summary of Reported Rates of Acidification

<table>
<thead>
<tr>
<th>Country</th>
<th>System</th>
<th>Acidification rate (kg lime ha(^{-1}) year(^{-1}))</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand</td>
<td>White clover-based pasture</td>
<td>75 to 90</td>
<td>Model calculation</td>
<td>De Klein et al. [27]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150 to 170</td>
<td>Based on pH change</td>
<td></td>
</tr>
<tr>
<td>New Zealand</td>
<td>White clover-based pasture</td>
<td>300 to 600</td>
<td>Based on amount of lime to maintain soil pH</td>
<td>Edmeades et al. [29]</td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Subterranean clover-based pasture</td>
<td>10 (no fertilizer) 70 (fertilizer) 140 (fertilizer + lime)</td>
<td>Based on pH change</td>
<td>Ridley et al. [30]</td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Subterranean clover-based pasture</td>
<td>100</td>
<td>Estimated from measurement of nitrate leaching and calculation of product removal</td>
<td>Ridley [31]</td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Perennial pasture</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Legume-based pasture</td>
<td>125 to 300</td>
<td>Based on pH change</td>
<td>Ridley and Coventry [32]</td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Legume-based pasture</td>
<td>5 to 180</td>
<td>Based on pH change</td>
<td>Helyar et al. [33]</td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Cereal–legume rotations</td>
<td>50 to 370</td>
<td>Based on pH change</td>
<td></td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Wheat</td>
<td>230</td>
<td>Based on pH change</td>
<td>Slattery et al. [34]</td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Lupins</td>
<td>625</td>
<td></td>
<td></td>
</tr>
<tr>
<td>United Kingdom</td>
<td>Not specified</td>
<td>195</td>
<td>Based on acid deposition</td>
<td>Johnston et al. [35]</td>
</tr>
<tr>
<td></td>
<td>Legume-based pasture</td>
<td>300 to 600</td>
<td>Model calculation</td>
<td>Kennedy [36]</td>
</tr>
<tr>
<td></td>
<td>Grass + N fertilizer</td>
<td>1400 to 1700</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
crease the availability of these nutrients, a plant response to liming cannot be assumed to be due solely to the alleviation of toxicity. Conversely, the full extent of acid soil toxicity cannot be determined until these other confounding effects are eliminated or accounted for.

While acknowledging that liming an acid soil can have many effects, including physical and biological (see Ref. 41 for a recent review), the most important nutritional problems on acid soils, at least over the range of soil pH normally encountered, are listed in Table 3.

Identifying which of these factors, either singly or in combination, are operating on a given soil can have a large impact on the amount of lime required for remedial action, as these mechanisms operate over different ranges in the soil pH continuum. For example, it is now known that many acid soils in New Zealand and Australia were Mo deficient, and large responses to liming in legume-based pastures were observed. When Mo deficiency was specifically diagnosed and its interaction with soil pH resolved, farmers could obtain similar yields with small inexpensive applications of Mo rather than large dressings of lime (see review in Ref. 17). The economic advantages, at least in the short term were obvious. Similarly, on soils where the primary factor limiting plant growth is Al toxicity, relat-

<table>
<thead>
<tr>
<th>Country</th>
<th>Soils</th>
<th>Field buffer capacity, lime (tonnes ha(^{-1}) (pH unit)(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand</td>
<td>Range of 36 from throughout NZ</td>
<td>5 to 15 (0 to 7.5 cm)</td>
<td>De Klein (personal communication) based on data from Edmeades et al. [24]</td>
</tr>
<tr>
<td>Australia</td>
<td>Range of 11 soils in NSW</td>
<td>1.1 to 2.6 (10 cm)</td>
<td>Hochman et al. [37]</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>Sands and loamy sands</td>
<td>6 (0 to 20 cm)</td>
<td>Goulding and Annis [38]</td>
</tr>
<tr>
<td></td>
<td>Sands and loamy silt loams</td>
<td>7 (0 to 20 cm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clay loams and clays</td>
<td>8 (0 to 20 cm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organic (100 to 250 g OM kg(^{-1}))</td>
<td>10 (0 to 20 cm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peats (&gt;250 g OM kg(^{-1}))</td>
<td>16 (0 to 20 cm)</td>
<td></td>
</tr>
</tbody>
</table>

OM, organic matter.
tively small inputs of lime to bring the soil pH up to about 5.5 are all that is required for near-maximum production [6,7].

The same logic must apply to Ca. Applying small amounts of Ca to remedy Ca deficiency will cost less, it is assumed, than applying lime to change the soil pH. There is evidence indicating that Ca deficiency may be more prevalent than previously acknowledged on tropical acid soils [39,42,43].

Most acid soils are also extremely P deficient, a problem usually exacerbated by the presence of active Fe and Al oxides. Large amounts of P fertilizer are required in addition to liming to make them productive. Although there is a large amount of literature on the effects of soil pH on soil P availability, much of it is conflicting and confusing. Two reviews [44,45] concluded that, despite common myth, liming does not frequently have beneficial effects on soil P availability, as distinct from its effect on changing the ability of the plant to reach already avail-

<table>
<thead>
<tr>
<th>Factor limiting plant growth</th>
<th>Effect of liming</th>
<th>Typical conditions of occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al and Mn toxicity</td>
<td>Increases soil pH and reduces amount of phytotoxic A1 and Mn</td>
<td>pH &lt; 5.5, acid parent material</td>
</tr>
<tr>
<td>Ca deficiency</td>
<td>Supplies Ca</td>
<td>Highly weathered soils with low effective cation exchange capacity (ECEC)</td>
</tr>
<tr>
<td>Mo deficiency</td>
<td>Increases pH and increases Mo availability</td>
<td>Many soils derived from sedimentary, granitic, and metamorphic parent material</td>
</tr>
<tr>
<td>N deficiency</td>
<td>Increases pH and enhances net mineralization of organic N</td>
<td>Moderate acidity (pH 5.5 to 6.2), high soil organic matter, temperate soils</td>
</tr>
<tr>
<td>P deficiency</td>
<td>Decreases P sorption, increases solubility of P/Al and Fe minerals, increases mineralization of organic P</td>
<td>Soils with pH &lt; 5.0 and high content of active Al and Fe to which fertilizer P applied. Otherwise rare</td>
</tr>
<tr>
<td>Induced deficiency (Zn and Mn)</td>
<td>Increases pH and decreases the availability of Zn and Mn</td>
<td>High soil pH (&gt; 6.5), soils with low field buffer capacity (e.g., sands and soils with low organic matter)</td>
</tr>
</tbody>
</table>
able P, by reducing Al or Mn toxicity or deficiency of N and Mo. Edmeades et al. [45] referred to these processes as type A or type B, respectively, and noted that it is frequently the type A processes that are inferred in the generalization that liming increases P availability but it is often data related to type B processes that are used as evidence.

These two types of processes are frequently confused [17,45], but their distinction is important. It is only when the type A processes are operating that liming can be used as a means of reducing fertilizer P inputs. On the other hand, where type B processes are operating, the efficiency with which applied fertilizer P is used can be greatly increased.

There is now a greater understanding of the dangers of overliming, particularly in relation to increasing the risk of Zn and Mn deficiency. Overliming in this respect does not necessarily mean liming to soil pH levels above 7.0, for these effects can and do occur on some soils at lower pH levels [27].

3 COMPONENTS OF THE DECISION PROCESS

Given the preceding discussion, it should be clear that decisions regarding the need for lime are not simple. There are now many questions and options to consider (Fig. 2). These are grouped in four components in Fig. 2. The first three components—the soil, the plant, and the system—deal with the biophysical aspects that need to be considered. The factors affecting the economics of liming make up the fourth component. But all of these decisions must be made within the context of the prevailing social and cultural attitudes. What might otherwise seem an obvious decision at the biophysical level can frequently be confused at the social and cultural levels.

3.1 The Soil

3.1.1 Soil pH × Depth Profile

The first question at the biophysical level, although not necessarily at the cultural level, is whether the acidity-induced factors limiting plant growth are present in the topsoil, subsoil, or both. This will determine whether lime should be surface applied or incorporated in the topsoil or subsoil.

Thus, the first step is to measure the soil pH and extractable Ca, Al, and Mn at various depths in the profile. In the first instance, it is suggested that the sampling depths should reflect the pedological horizons, but it is noted that soil acidification can be stratified over a small scale (20 to 40 mm) within the soil horizon [46]. It is also desirable to use methods that reflect the prevailing ionic strength of the soil solution [18–20].

Sumner [40] provided examples of the pH and Al profiles of eight soils and distinguished between two groups, depending on the acidity of the parent material...
and the subsequent acidification due to management practices. Soils in the first group, referred to here as group 1, are typically from tropical and humid subtropical regions. They have naturally acid topsoils and subsoils, some of which have become more acid through management practices. They generally have a large component of variable charge, and their pH and effective CEC decrease with increasing soil depth. These soils are likely to exhibit both Al toxicity and Ca deficiency.

**Figure 2** A process for deciding on the biophysical need for lime.
The second group (group 2) comprises soils from subhumid, subtropical, and tropical regions and humid temperate regions. They do not normally have subsoils acid enough to limit root growth but may have developed acid topsoils due to acidifying management practices. They have less variable charge, a higher effective CEC, and are unlikely to be Ca deficient. For these soils, pH increases with increasing depth.

Helyar [47] emphasized the same soil-forming factors, parent material, weathering, and subsequent management in describing the types of soil pH profiles typically found in New South Wales (NSW), Australia (Fig. 3). There are

![Soil pH profiles](https://example.com/soil_pH_profiles.png)

**Figure 3** Soil pH profiles typical of the soil types in NSW, Australia. (From Ref. 47.)
other examples of soil pH profiles in the literature (Adams [5], 4 soils in southern United States: Scott et al. [46], 15 sites in southeastern Australia: Moody and Aitken [48], 4 sites in Queensland, Australia: Wheeler [49], 12 sites in the North Island, New Zealand; Farina et al. [50], 1 site, South Africa).

Soil pH profiles can change significantly over time due to management practices. Moody and Aitken [48] measured the long-term consequences of three management systems for soil pH profiles in Queensland. Similarly, Adams [5] gave examples of the short-term effects (5 years) of Bermuda grass, fertilized with N. These are all group 1 soils, using Sumner’s [40] definition, and in all cases there was net acidification.

Other studies have examined the long-term effects of management practices on group 2 soils. For example, Ridley et al. [30] examined the effects of 73 years of legume-based pasture on the soil pH profile. In the absence of lime, this system had a net acidifying effect. Wheeler and Addison [51] resampled 35 reference sites in New Zealand, 30 years after they were first sampled and analyzed. Fifteen of the original sites remained under legume-based pasture and were subject to the normal agricultural practices, including possibly liming. For 7 of the 15 sites, there was net acidification equivalent to a decrease in pH of 0.43 units. The pH of the other 8 sites increased by 0.40 units. There can be no doubt that the processes that contribute to soil acidification, including product removal, organic matter accumulation, and nitrate leaching, are occurring to varying extents on these soils. It is reasonably assumed, therefore, that the absence of acidification on half of these sites is due to topsoil liming, as widely practiced in New Zealand legume-based pastures.

Comparing new soil pH profiles with these examples could provide useful insights into future management and appropriate liming strategies.

3.1.2 Determining the Primary Growth Limiting Factor

Any decision about lime application must also take into account the nature of the acidity—what is the primary factor limiting plant growth? As previously discussed, the answer to this question can have a profound effect on the amount of lime required to maximize production. However, it is difficult to make an unambiguous diagnosis because all liming experiments are confounded. It is impossible to alter one soil acidity constraint without simultaneously altering others. Because of this, liming experiments need to be carefully designed to eliminate all the possible confounding effects and hence deduce the mostly likely limiting factor. Applications of trace elements and fertilizer N should eliminate the possibility that these nutrients are confounding factors. Measuring the response to lime in the presence and absence of applied P and Ca (as a neutral salt) and examining their interactions can assist in separating the effects of liming on Ca deficiency and soil P availability from those due to Al toxicity per se. Plant analysis can also be useful, especially for diagnosing Mn toxicity and Mo and Ca deficiency. For a more thorough discussion, see Edmeades et al. [17] and for examples of the approach
required see Adams and Moore [42], Bruce et al. [43], Edmeades et al. [45], Black [2], and Wheeler et al. [52].

3.1.3 Soil Buffer Capacity

The field buffer capacity is essential for prescribing the amount of lime required to achieve the optimal pH (see Sec. 3.3.1). It is also required to predict the effect of ongoing acidification on soil pH.

Based on data from 36 field trials [24] on temperate soils in New Zealand, De Klein (personal communication) has calculated field buffer capacities of between 100 and 300 (average 170) kmole ha\(^{-1}\) (pH unit)\(^{-1}\) [5 to 10 tonnes ha\(^{-1}\) (pH unit)\(^{-1}\)] (Table 2). They were not related to the soil properties CEC, total exchangeable bases, organic matter, soil texture, and extractable Al.

In the UK, “lime factors” have been derived empirically and are related to soil texture and topsoil depth. Figures range from 4.5 tonnes ha\(^{-1}\) (pH unit)\(^{-1}\) on sandy grassland soils (0 to 15 cm depth) to 16 for arable organic soils (0 to 20 cm depth) [38].

Hochman et al. [37] used the term lime responsiveness index to describe the change in topsoil (10 cm) pH 1 year after lime application in 13 field experiments in NSW Australia. Figures ranged from 1.1 to 2.5 tonnes ha\(^{-1}\) (pH unit)\(^{-1}\). Because of the short duration of the trials, these are likely to overestimate the real buffer capacity, but what is interesting is that they could be predicted based on the initial pH, total exchangeable cations, organic matter, and extractable Al. More work of this type is desirable to determine whether soil field buffer capacities can be readily predicted from simple soil measurements.

Although it would be desirable to develop a laboratory test to estimate the field buffer capacity, the history of lime research indicates the futility of this approach [3,5,24,32,40,53]. In any case, the buffer capacity of a soil in situ can be determined readily at little expense. The only requirements are a field trial with several rates of lime, a pH meter, and annual sampling and measurement of soil pH over a long period of time (3 to 5 years).

3.2 The Plant

3.2.1 Size of Lime Responses

The striking features of the international data on plant responses to liming are the wide range of reported responses for a given crop and the size of the largest responses (Table 4). The exceptions appear to be the pasture responses to liming on mineral soils in New Zealand.

Such data are difficult to interpret and are therefore of limited value. Most reviewers, while noting these very positive effects, emphasize the unpredictable nature of the responses. The difficulty, as Sumner [21] noted, is that the conditions under which most of these field trials were conducted have not been recorded in
### TABLE 4  Range and Typical Responses of Crops and Pastures to Surface Application of Topsoil Incorporated Lime

<table>
<thead>
<tr>
<th>Country</th>
<th>Crop (soil type)</th>
<th>Soil acidity</th>
<th>Absolute range and typical range(^a) of response to lime (% relative to control)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand</td>
<td>White clover-based pasture (mineral soils)</td>
<td>pH(_W) 5.0 to 6.0</td>
<td>0 to 10 (about 5)</td>
<td>Edmeades et al. [22]</td>
</tr>
<tr>
<td></td>
<td>Clover-based pasture</td>
<td>pH(_W) 4.0 to 5.0</td>
<td>10 to 140 (50 to 100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organic soils</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australia</td>
<td>Subterranean clover-based pasture</td>
<td>pH(_C) 4.2 to 4.7</td>
<td>−15 to 170 (20 to 60)</td>
<td>Scott et al. [46]</td>
</tr>
<tr>
<td>NSW, Vic</td>
<td>Phalaris pastures</td>
<td>pH(_C) 4.1 to 5.0</td>
<td>0 to 900 (30 to 100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cocksfoot pastures</td>
<td>pH(_C) 4.1 to 5.0</td>
<td>0 to 70 (about 20)</td>
<td></td>
</tr>
<tr>
<td>Australia</td>
<td>Wheat</td>
<td>pH(_W) 5.0 to 6.0</td>
<td>0 to 38</td>
<td>Coventry et al. [54]</td>
</tr>
<tr>
<td>NSW, Vic</td>
<td>Corn</td>
<td>pH(_W) 5.0 to 5.4</td>
<td>0 to 400 (10 to 30)</td>
<td>Adams [5], Adams and Pearson [55]</td>
</tr>
<tr>
<td></td>
<td>Soybean</td>
<td>pH(_W) 4.7 to 5.5</td>
<td>11 to 56 (10 to 30)</td>
<td></td>
</tr>
<tr>
<td>United States</td>
<td>Soybean</td>
<td>pH(_W) 4.7 to 5.8</td>
<td>0 to 56 (30 to 50)</td>
<td></td>
</tr>
<tr>
<td>southern</td>
<td>Alfalfa</td>
<td>pH(_W) 4.7 to 5.8</td>
<td>150 to &gt;1000 (100 to 200)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other forage crops(^b)</td>
<td>pH(_W) 4.3 to 5.5</td>
<td>0 to 250 (10 to 30)</td>
<td></td>
</tr>
<tr>
<td>United States</td>
<td>Corn</td>
<td>pH(_W) 5.0</td>
<td>75 to 96(^c)</td>
<td>McLean and Brown [56]</td>
</tr>
<tr>
<td>midwest</td>
<td>Soybean</td>
<td>pH(_W) 5.0</td>
<td>70 to 91(^c)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alfalfa</td>
<td>pH(_W) 5.0</td>
<td>20 to 84(^c)</td>
<td></td>
</tr>
<tr>
<td>Various(^d)</td>
<td>Soybean</td>
<td>A1 base saturation 75%(^f)</td>
<td>25 to 95(^g)</td>
<td>Dierolf et al. [57]</td>
</tr>
<tr>
<td></td>
<td>Corn</td>
<td>A1 base saturation 75%(^f)</td>
<td>66 to 95(^g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Various(^e)</td>
<td>A1 base saturation 75%(^f)</td>
<td>80 to 95(^g)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Typical value by visual inspection of the data.

\(^b\) White clover, crimson clover, bermudagrass, millet, sorghum, ryegrass.

\(^c\) Response at pH 5.0 relative to maximum yield.

\(^d\) All tropical soils (Oxisols and Ultisols) from 10 countries.

\(^e\) Groundnut, rice, cowpea, mungbean, pigeon pea, cassava, tanier, yams, sugarcane.

\(^f\) Al base saturation % of ECEC.

\(^g\) Response at Al saturation of 75%, relative to maximum yield.
Using Lime to Ameliorate Acidity

It has been known for a long time that plant species differ in their tolerance to soil acidity [61]. Most early textbooks (e.g., Russell [3]) provided tables of the relative tolerance of different species to soil acidity. However, a species that is tolerant to acidity at one site may not necessarily thrive on another acid soil. The specific cause of the acid infertility, and the plant’s adaptation to it, needs to be identified and linked before such information can be used generally [62]. Also, large genotypic variability within species can result in overlapping in acid tolerance between species. Thus, such lists (Table 5) must be treated cautiously.

Much research has been directed to exploiting this variability to develop acid-tolerant species and cultivars, and today it is possible to be more specific and rank species according to their tolerance to one specific acid soil constraint, such as Al toxicity (Table 5) or Mn toxicity (see Chapter 10). With information such as this, it is now possible to choose species and cultivars that are better adapted to the prevailing soil conditions. This has become the basis for developing low-cost options for maintaining and increasing plant production on acid soils. However, this approach is limited by the range of tolerance that can be introduced into the important food plants.

Furthermore, using acid-tolerant species does not mean that lime will no longer be required. Soils will continue to acidify even when tolerant species are
### TABLE 5  Aluminum Tolerance of Some Crops and Pasture Plants

<table>
<thead>
<tr>
<th>Aluminum tolerance category</th>
<th>Plant species/cultivar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly sensitive</td>
<td>Alfalfa</td>
</tr>
<tr>
<td></td>
<td>Most annual medics</td>
</tr>
<tr>
<td>Sensitive</td>
<td>Canola</td>
</tr>
<tr>
<td></td>
<td>Some wheats</td>
</tr>
<tr>
<td></td>
<td>Most barley</td>
</tr>
<tr>
<td></td>
<td>Buffel grasses</td>
</tr>
<tr>
<td></td>
<td>Most phalaris genotypes</td>
</tr>
<tr>
<td></td>
<td>Lespedeza*</td>
</tr>
<tr>
<td></td>
<td>Cotton*</td>
</tr>
<tr>
<td></td>
<td>Sorghum*</td>
</tr>
<tr>
<td></td>
<td>Soybean*</td>
</tr>
<tr>
<td></td>
<td>Tobacco*</td>
</tr>
<tr>
<td>Tolerant</td>
<td>Rye grasses</td>
</tr>
<tr>
<td></td>
<td>Tall fescue</td>
</tr>
<tr>
<td></td>
<td>White clover</td>
</tr>
<tr>
<td></td>
<td>Some cocksfoots (orchard grass)</td>
</tr>
<tr>
<td></td>
<td>Some wheats</td>
</tr>
<tr>
<td></td>
<td>Subterranean clover</td>
</tr>
<tr>
<td></td>
<td>Albus lupins</td>
</tr>
<tr>
<td></td>
<td>Dallisgrass*</td>
</tr>
<tr>
<td></td>
<td>Corn*</td>
</tr>
<tr>
<td></td>
<td>Rice*</td>
</tr>
<tr>
<td></td>
<td>Peanuts* (except to low Ca)</td>
</tr>
<tr>
<td>Highly tolerant</td>
<td>Some cocksfoots (orchard grass)</td>
</tr>
<tr>
<td></td>
<td>Pioneer rhodes grass</td>
</tr>
<tr>
<td></td>
<td>Some lovegrasses</td>
</tr>
<tr>
<td></td>
<td>Paspalum</td>
</tr>
<tr>
<td></td>
<td>Kikuyu</td>
</tr>
<tr>
<td></td>
<td>Maku lotus</td>
</tr>
<tr>
<td></td>
<td>Narrow-leaf lupins</td>
</tr>
<tr>
<td></td>
<td>Slender serradella</td>
</tr>
<tr>
<td></td>
<td>Most oats</td>
</tr>
<tr>
<td></td>
<td>Most triticale</td>
</tr>
<tr>
<td></td>
<td>Yellow serradella</td>
</tr>
<tr>
<td></td>
<td>Cereal rye*</td>
</tr>
<tr>
<td></td>
<td>Bermuda grass*</td>
</tr>
<tr>
<td></td>
<td>Bahia grass*</td>
</tr>
</tbody>
</table>

*Source: Ref. 46 or Ref. 5 for those marked*. 
used. This will mean that either increasing tolerance will need to be bred into the important cropping species or, at some point, liming will need to be introduced into the management system. For these reasons more, not less, emphasis should be given to liming soils as the long-term solution to acid soil infertility.

3.2.3 Acid Tolerance and Drought Tolerance

There is an important interaction between plant tolerance to soil acidity, in particular Al toxicity, and tolerance to moisture stress. This interaction can cause confusion and can be a confounding factor in plant responses to liming in the field.

It has long been known that Al toxicity inhibits root growth [63]; there are many examples of this phenomenon in the literature. Thus, a plant exposed to Al toxicity also exhibits intolerance to moisture stress because the root system is unable to exploit fully soil moisture reserves [5,39,40].

Perennial plants can adapt to moisture stress by adjusting their perenniality. For example, annuals can escape moisture stress by “dying” over the summer period. If such a plant is grown on an acid soil and at the same time is exposed to moisture stress, it may appear as if it is tolerant to acidity when in fact its survival is not related to an adaptation to acidity.

The problem becomes even more complex when naturally deep-rooted plants, which may or may not be acid tolerant, are grown on soils with either acid topsoils or subsoils. The effects of these various combinations on the likely response to liming are explored conceptually in Table 6. For example, a sensitive species (such as lucerne or canola) is likely to be very responsive to liming if topsoil acidity is the only limitation. Conversely, the expected response would be small for acid-tolerant crops such as cereal rye or oats. If a soil had strongly acid subsoil, then a sensitive and deep-rooted species such as lucerne would not respond well to topsoil amelioration. This interaction between acid tolerance, drought tolerance, and rooting depth could be a major source of variation in plant responses to lime, as discussed in Sec. 3.2.4.

3.3 The Agricultural System

3.3.1 The Biological Lime Requirement

Using Black’s [2] definition, the biological lime requirement (BLR) can be defined for a given soil and crop as

\[
\text{BLR (tonnes ha}^{-1}) = (\text{optimal pH} - \text{current pH}) \times \text{BC (tonnes (pH unit})^{-1}))
\]

where the optimal pH is the soil pH required for the specific crop or cropping system, the current pH is the pH of the topsoil, and the buffer capacity (BC) is the amount of lime (tonnes) to increase the pH of the topsoil by 1 unit. This is only
the amount of lime required to achieve the optimal pH and does not consider how much lime is required to maintain the optimal pH. The maintenance lime requirement (MLR) can be defined as

\[
\text{MLR} (\text{kg ha}^{-1} \text{ year}^{-1}) = \text{acidification rate (kmoles H}^+ \text{ ha}^{-1} \text{ year}^{-1}) \times 50
\]

The acidification rate can either be determined using one of a number of models [26,27] or estimated from published data. A summary of available data was given in Table 1.

The quality of the lime can readily be factored into these calculations provided its lime equivalence is known. The hardness and the particle size of the lime also need to be considered, but these factors are more relevant to how quickly and how long the effects of liming will last. They will be dealt with later (Secs. 3.3.2. and 3.3.3.).

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Plant tolerance to acidity</th>
<th>Rooting depth</th>
<th>Likely lime response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid topsoil only</td>
<td>Acid sensitive</td>
<td>Shallow</td>
<td>Large response</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deep</td>
<td>Large response</td>
</tr>
<tr>
<td></td>
<td>Moderately tolerant</td>
<td>Shallow</td>
<td>Nil or small response</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deep</td>
<td>Nil or small response</td>
</tr>
<tr>
<td>Acid topsoil and subsoil</td>
<td>Acid sensitive</td>
<td>Shallow</td>
<td>Response dependent upon depth of root extension into subsoil without acid soil limitation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deep</td>
<td>No response, poor growth</td>
</tr>
<tr>
<td></td>
<td>Moderately tolerant</td>
<td>Shallow</td>
<td>Small response</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deep</td>
<td>Moderate response if liming of topsoil markedly increased root proliferation and thus nutrient access</td>
</tr>
</tbody>
</table>

*a Shallow rooting depth—it is assumed that roots are largely confined to the topsoil, whereas deep rooted is assumed to mean that roots extend well into the subsoil.

*b It is assumed that sufficient lime has been applied to overcome the soil acidity limitation of most or all of the topsoil.
3.3.2 Placement of Lime

The placement of lime is important because it affects how quickly, to what depth, and over what period of time the effects of lime are required. The option chosen—surface application, topsoil incorporation, and/or subsoil amelioration—will depend on the answers to these questions.

Two reviews [40,46] have discussed the various mechanisms—chemical, biological, and physical—by which surface-applied and surface-incorporated lime could affect soil acidity below the level of incorporation. Both concluded, however, that the accumulated results were too variable to reach a definitive conclusion in terms of how far the effects of liming penetrated down the profile. This view needs challenging.

Lime is a relatively insoluble material and the products of liming, alkalinity in the form of \( \text{OH}^- \), \( \text{HCO}_3^- \), and \( \text{CO}_3^{2-} \), move through the soil slowly, taking many years. This is readily accepted for the reverse process, anthropogenic acidification, but nevertheless data from short-term trials are frequently used to test the hypothesis that lime does or does not move into the soil beyond the depth of placement [40,46].

The data from Sumner [40] and Scott et al. [46] are reassessed in Table 7, using only the data from trials that went for >10 years and adding other examples from the literature. In all cases, liming affected the soil below the level of placement. These results should not be taken to imply that it takes at least 10 years for surface liming to affect the subsoil. The data in Table 7 have simply been selected to demonstrate that the effects of liming below the level of incorporation occur slowly and that it is inappropriate to reject the hypothesis on the basis of short-term trials.

Other examples from the literature demonstrate quicker effects. In New Zealand, Doak [70] found that liming at 2 tonnes ha\(^{-1}\) (rainfall 800 mm) increased the pH at 15 to 25 cm, 2 years following liming, and that the maximum effect at this depth occurred 4 years after surface application (Fig. 4). Wheeler [64] reported similar results under almost identical circumstances. The maximum effect of surface-applied lime on soil pH occurred 2, 5, 12, and 15 years for the depths 0 to 50, 50 to 100, 100 to 150, and 150 to 200 mm, respectively, following surface application of 7.5 tonnes lime ha\(^{-1}\). At higher rainfall (1500 mm year\(^{-1}\)) the effects are even quicker (Fig. 5) [49].

Similarly, in Australia, Ridley and Coventry [32] reported increased pH in the 100 to 2000 mm depth 5 years after surface incorporation (100 mm) of 5 tonnes ha\(^{-1}\) (rainfall 800 mm year\(^{-1}\)). Conyers and Scott [71] found substantial increases in pH below the depth of incorporation 5 years after application of 8 tonnes lime ha\(^{-1}\). Two tonnes ha\(^{-1}\) had no effect below the depth of incorporation.

It is concluded, therefore, that surface liming, and the incorporation of lime into the topsoil, can and does reduce soil acidity below the depth of incorporation,
<table>
<thead>
<tr>
<th>Location</th>
<th>Soil</th>
<th>Lime rate (t ha(^{-1}))</th>
<th>Lime placement</th>
<th>Duration (years)</th>
<th>Depth of effect (cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand</td>
<td>Pallic</td>
<td>7.5</td>
<td>Surface</td>
<td>15</td>
<td>20</td>
<td>Wheeler [64]</td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Granite</td>
<td>3.6</td>
<td>Surface</td>
<td>10</td>
<td>20</td>
<td>Cumming [65]</td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Basalt</td>
<td>5.0</td>
<td>Surface</td>
<td>10</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Red earth</td>
<td>5.5</td>
<td>Surface</td>
<td>13</td>
<td>20</td>
<td>Horsnell [66]</td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Red earth</td>
<td>3.3</td>
<td>Surface</td>
<td>13</td>
<td>15–30</td>
<td></td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Yellow duplex</td>
<td>3.6</td>
<td>Incorp. 10 cm</td>
<td>12</td>
<td>20–30</td>
<td>Broemfield et al. [67]</td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Yellow duplex</td>
<td>5.6</td>
<td>Incorp. 10 cm</td>
<td>12</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Red earth</td>
<td>3.3</td>
<td>Incorp. 5 cm</td>
<td>13</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Australia NSW</td>
<td>Red earth</td>
<td>5.5</td>
<td>Incorp. 5 cm</td>
<td>13</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Australia Vic</td>
<td>Yellow podzolic</td>
<td>11.25</td>
<td>Surface</td>
<td>40</td>
<td>50</td>
<td>Ridley et al. [30]</td>
</tr>
<tr>
<td>South Africa</td>
<td>Plinthic paleudult</td>
<td>25</td>
<td>Incorp. topsoil</td>
<td>11</td>
<td>?</td>
<td>Farina et al. [50]</td>
</tr>
<tr>
<td>United States,</td>
<td>Typic dystrochrept</td>
<td>16</td>
<td>Incorp. topsoil</td>
<td>20</td>
<td>50</td>
<td>Brown et al. [68]</td>
</tr>
<tr>
<td>Connecticut</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>United States,</td>
<td>Typic dystrochrept</td>
<td>10</td>
<td>Incorp. topsoil</td>
<td>18</td>
<td>90</td>
<td>Brown and Munsell [69]</td>
</tr>
<tr>
<td>Alabama</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>United States,</td>
<td>Not given</td>
<td>0.5 and 0.8 annually</td>
<td>Incorp. topsoil</td>
<td>32</td>
<td>45–60</td>
<td>Adams [5]</td>
</tr>
<tr>
<td>Alabama</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>United States,</td>
<td>Not given</td>
<td>0.5 and 0.8 annually</td>
<td>Incorp. topsoil</td>
<td>32</td>
<td>45–60</td>
<td></td>
</tr>
</tbody>
</table>
given sufficient input of lime and, significantly, sufficient time. This conclusion is not new and supports the view recorded by Adams [5] that one obvious solution to subsoil acidity is topsoil liming. It is also noted that anthropogenic acidity can occur over small depths within the topsoil [46], well within the reach of surface-applied ameliorants.

FIGURE 4  Effect of time on the change in soil pH at four soil depths following the application of lime (5 tonnes ha$^{-1}$); 0–50 mm (squares), 50–100 mm (circles), 100–150 mm (triangles), 150–250 mm (crosses). (Modified from Ref. 70.)

FIGURE 5  Effect of rate of lime application on the change in soil pH at four soil depths. Rates of lime (tonnes ha$^{-1}$); 10 (squares), 7.5 (circles), 5.0 (triangles), 2.5 (crosses), 1.25 (diamonds). (Modified from Ref. 49.)
Several qualifications are, however, required. If the mechanism by which liming affects the subsoil is chemical [40], then this conclusion requires that there are no long-term impediments to the vertical flow of water through the soil to carry by mass action the soluble products of liming—\( \text{CO}_3^{2-}, \text{HCO}_3^{-}, \text{and OH}^- \).

Lime in excess of that required to neutralize the surface or topsoil acidity is required for amelioration of subsoil acidity. Sumner [40] suggested that the topsoil pH would need to be well above 5.6 for a sufficient amount of mobile alkalinity to be present. This is certainly consistent with the measurements made by Wheeler and Edmeades [72]. They found that the pH of the soil solution 2 years following the application of lime (7.5 tonnes ha\(^{-1}\)) was above 7.5 (unlimed 6.4) and the bicarbonate concentration was about 20 \(\mu\text{M}\) (unlimed 2 \(\mu\text{M}\)). Sumner [40] also noted that soils with variable charge minerals in their subsoils would consume more alkali than soils with predominantly permanent charged minerals.

Sumner [40] suggested that the rate at which alkalinity moves into the soil may be related to whether Ca and Mg or Na was accompanying the alkali anions. It is interesting to note that Na rather than Ca or Mg is the dominant cation in most soil solutions [17].

The question of where lime should be placed reduces to one of time. Based on first principles, the time required will depend on (1) the amount of water passing through the topsoil, (2) the concentration of alkalinity in the topsoil, (3) the relative concentrations of accompanying cations, (4) the presence of macropores, and (5) the presence of burrowing soil fauna such as earthworms.

If time is of little consequence, as is the case when land is still relatively productive and lime is required simply to offset the current rate of acidification and maintain the current top and subsoil pH, then there is little purpose in doing other than applying lime to the surface. If cropping, then it is relatively inexpensive to incorporate lime into the topsoil during cultivation. If the cropping program is undertaken using zero tillage, then obviously the lime must be surface applied.

If the acid infertility problem lies below the effective “plow” layer for surface incorporation, there are other options. If there is an urgent need for remedial action, then subsoiling is the only option. Sumner [40] has reviewed the various techniques and results. He concluded that the evidence showed clear benefits to deep liming in terms of subsequent root proliferation and hence yield but questioned the practice on economic grounds.

Farina et al. [50] have reported the results of a long-term experiment (11 years) comparing various strategies for ameliorating subsoil acidity. A summary of their results is given in Table 8. Economic analysis (Fig. 6) showed that the best lime incorporation treatments, in terms of plant responses, were cost effective in the long term. Appreciating that such analyses are specific at a regional and crop and possibly site level, they are nevertheless important in the general context because they challenge conventional wisdom. More long-term trials of this nature are required so that the biological basis for long-term economic analysis can be as-
It is noted, however, that deep liming with lime incorporation is common practice on very acid peat soils [22,73].

If time is not a factor, then many cases of subsoil acidity could be solved by initial high capital inputs of lime to the topsoil followed by maintenance inputs as discussed earlier. The long-term economics of this strategy have yet to be investigated, and it is likely that the biological information required for such an assessment is also not available.

### TABLE 8

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield (tonne ha(^{-1})) of corn grain and silage (mean over 11 seasons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional moldboard incorporation (10 tonnes lime ha(^{-1}) to 25 cm)</td>
<td>5.4</td>
</tr>
<tr>
<td>Deep moldboard incorporation (10 tonnes lime ha(^{-1}) to 50 cm)</td>
<td>6.2</td>
</tr>
<tr>
<td>Gypsum (5 tonnes ha(^{-1})) incorporated to 25 cm after conventional moldboard incorporation (10 tonnes ha(^{-1}) to 25 cm)</td>
<td>6.7</td>
</tr>
</tbody>
</table>

*Source: Adapted from Ref. 50.*

FIGURE 6  Effect of deep moldboard lime incorporation (10 tonnes ha\(^{-1}\), 50 cm, squares) and surface incorporation of gypsum (5 tonnes ha\(^{-1}\), 25 cm, circles) on annual profit or loss from corn grain, relative to conventional moldboard incorporation (10 tonnes ha\(^{-1}\), 25 cm) (no data were collected in year 10). (Modified from Ref. 50.)
Other options such as the use of gypsum or changing land use are beyond the scope of this chapter.

3.3.3 Longevity of the Liming Effect

The traditional liming strategy is to apply sufficient lime in a single application to achieve a specified target pH and to reapply further lime when required. In practice, this is normally determined by monitoring the pH over time. But the economics of liming are very dependent on the duration of the effect on plant production. It is desirable therefore to be able to predict the duration of the effects of liming. Once again, despite the importance of this factor, very few data are available.

Black [2] cites an example from a field trial in the UK showing the effect of time after liming on the soil pH. Edmeades et al. [22] used data like this from long-term trials in New Zealand to model the duration of the liming effect based on rainfall and the rate of application. The higher the rate of application and the lower the rainfall, the longer the duration. For example, the effects of surface application of 2.5 tonnes ha\(^{-1}\) lime were given by

\[
\text{Duration (years)} = 9 - [0.0012 \times \text{annual rainfall (mm)}]
\]

Thus, the duration is about 8 years at 500 mm annual rainfall, decreasing to 6 years at 2000 mm. These figures generally agree with practical experience in New Zealand and in Victoria, Australia.

Symth and Cravo [74] related the Al saturation of the soil, expressed as the proportion of effective cation exchange capacity (ECEC), to the rate of application of lime (\(r\)) and time (\(t\)) since application, based on trials from Brazil. Aluminum saturation decreased with an increasing rate of lime application and increased with time according to the relationship

\[
\text{Al saturation} = 58.3 - 20.2r + 1.6r^2 + 2.1t + 1.1t^2
\]

Dierolf et al. [57] subsequently validated this relationship with data from other trials whose duration ranged from 40 to 68 months.

Hockman et al. [37] used a different approach and calculated the residual value of lime based on observed rates of reacidification in the field after liming. They related the pH at time (\(t\)) to the initial virgin soil pH (pH\(_v\)) for a soil with a buffer capacity (BC\(_s\)) according to the relationship

\[
\text{pH}_v = 2.42 + (\text{pH}_v - 2.42) \times e^{-0.0058 \times t \times BC_s}
\]

Like field buffer capacity, the duration of the effect of liming is a vital piece of information required to make liming decisions. Hence, more long-term trials are required. Also, if it is assumed that the duration of the effect of lime on plant growth will be related to its effect on pH, such trials need not be expensive to conduct.
3.3.4 Quality of Lime

There are three important components to lime quality—lime equivalence or neutralizing value, particle size, and hardness—the latter being determined largely by the chemical composition of the lime. The impact of these three factors on the effectiveness of liming materials is reviewed elsewhere [2,75], and Goulding and Annis [38] provide a recent summary of research in Britain.

Conyers et al. [76], working with 12 liming materials from NSW, Australia, defined the relative physical efficiency (essentially the particle size) and the relative chemical efficiency (lime equivalence and chemical composition). They found good agreement between the measured and actual total efficiency (the product of the physical and chemical efficiency) as measured in the field.

Although lime quality can vary considerable from location to location, transport costs normally dictate the choice of lime. In any case, a fine, soft, fast-acting lime will have a shorter residual effect than a coarser, harder material. The key is to match the lime quality with the intended use. Many products will be suitable if required for a maintenance program. A fast-acting lime is required where there is an urgent need to increase the soil pH.

3.4 The Economics of Liming

The economics of liming depend on the size of the benefits accruing from liming relative to the cost of liming. The benefits are a function of the size and value of the plant response plus the duration of the liming effect. The costs include the purchase, transport, and spreading of lime.

A cost–benefit analysis can readily be done at an individual site, provided the size and duration of the effect of liming are known, together with the costs. But such information is not transferable to another site unless the size and duration of the plant response to liming can be predicted. In essence, what are required are the production functions for different crops relating the degree of soil acidity, whether measured as soil pH or some other criteria, to the size and duration of the likely plant response.

Slow progress is being made to this end. Edmeades et al. [22] found relationships between soil pH and the size of pasture responses to lime, applied at three rates. This information, coupled with a simple model to predict the duration of pasture responses to liming from the rainfall data, forms the basis of the econometric lime model, the AgResearch PKSLime Program (NZ Pastoral Research Institute Ltd), currently used to offer advice to farmers.

Results are reported, for a given set of farm input data, in terms of the net present value (NPV—the sum of the annual financial benefits per year, for the duration of the response, expressed in current dollar terms) for each potential rate of lime application. The combination of soil pH and stocking rate for which the NPV is positive (liming economic) or negative (liming not economic) is shown in Fig.
7. For this set of input data, it would not be economic to use lime if current soil pH is greater than 5.5 and the stocking rate $<10$.

Similarly, in Australia, Hochman et al. [60] have developed a decision support software system (DSSS) called “Lime-It.” In this case, the important production functions are the relationships between soil pH and relative yield for a number of different crops and pastures.

Dierolf et al. [57] have reported the development of an Acidity Decision Support System (ADSS). This is being developed for highly weathered mineral soils for which the sole factor limiting plant growth is Al toxicity. The production functions are the relationships between crop yield and the degree of Al saturation in the soil.

Hochman et al. [60] emphasized the importance of the ratio of the cost (of lime) to value (of the agricultural product) in determining the economics of liming (Table 9). In countries and farming enterprises where the cost/value ratio is low, such as for corn in Alabama, potatoes in The Netherlands, and dairy pastures...
in New Zealand, liming acid soils can be highly profitable. In contrast, for enterprises such as livestock production and to a lesser extent cereal cropping in southern Australia, liming is economic only under certain circumstances and often requires excellent management skills in other aspects of the farming enterprise to be so. To some extent, these data explain why the use of lime is more prevalent in some countries than in others.

Undoubtedly, the cost/value ratio does affect the economics of liming, but this masks the most important determinants—the size and duration of the plant response to liming. This is illustrated in Fig. 8. Using the AgResearch PKSLime Program, the effect of altering the cost/value ratio (by adjusting the cost of transporting the lime from NZ$10 to NZ$100 per tonne) on the NPV of liming on an average dairy pasture in New Zealand has been determined at two different lime response levels—2 to 3% and 10 to 12%. In this case, the size of the response, determined by the initial soil pH, has a major influence on the economic outcome. Given that the sizes of many reported crop responses to liming are much greater

<table>
<thead>
<tr>
<th>Crop</th>
<th>Location</th>
<th>Value production (US$ ha(^{-1}) year(^{-1}))</th>
<th>Cost of lime at 2.5 t ha(^{-1}) (US$)</th>
<th>Cost/value (x100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa (for hay)</td>
<td>Mayfield, Kentucky</td>
<td>260</td>
<td>33</td>
<td>12.7</td>
</tr>
<tr>
<td>Soybean</td>
<td>Crossville, Alabama</td>
<td>595</td>
<td>33</td>
<td>6.5</td>
</tr>
<tr>
<td>Corn</td>
<td>Southern Coastal Plain, Virginia</td>
<td>740</td>
<td>33</td>
<td>4.5</td>
</tr>
<tr>
<td>Winter wheat</td>
<td>Central clay area, Netherlands</td>
<td>3551</td>
<td>380</td>
<td>10.7</td>
</tr>
<tr>
<td>Potatoes</td>
<td>Central clay area, Netherlands</td>
<td>9450</td>
<td>380</td>
<td>4.0</td>
</tr>
<tr>
<td>Dairy pasture</td>
<td>Volcanic ash soils, New Zealand</td>
<td>460</td>
<td>42</td>
<td>9.1</td>
</tr>
<tr>
<td>Sheep pasture</td>
<td>‘Easy Hill Country’, King Country, New Zealand</td>
<td>300</td>
<td>71</td>
<td>23.7</td>
</tr>
<tr>
<td>Pasture for sheep</td>
<td>Southern slopes, New South Wales, Australia</td>
<td>211</td>
<td>150</td>
<td>71.1</td>
</tr>
<tr>
<td>Wheat</td>
<td>Wagga Wagga, New South Wales, Australia</td>
<td>264</td>
<td>150</td>
<td>56.8</td>
</tr>
</tbody>
</table>

Source: Adapted from Ref. 6.0.
than used in this example (Table 4), it is surprising that liming is so frequently dis-
missed as uneconomic.

Similarly, the duration of the response (Sec. 3.3.2) also has a major impact on the economic outcome of liming. The reason for this is that the initial one-off cost of liming is spread over the duration of the response to liming. In New Zealand, this can range from 4 to 10 years.

Given their importance in determining the economic outcome of liming, more basic research is required to define these parameters across the range of soils and crops of economic value. Until such work is done, it should not be asserted that liming acid soils is not economic and that, therefore, the only solution to acid soil infertility is to find other nonliming remedies (for example, see Ref. 46). This will require a change in attitude and hence science direction.

3.5 Social Issues

Lime is most commonly applied on acid soils in industrialized countries [77]. It is technically and economically feasible to lime acid soils in such countries. But in other countries, the successful management of acid soils depends upon integrating the technical issues with social and economic factors [62]. Social factors can be pivotal reasons why some people may choose not to lime before even considering
economic or biophysical factors. Issues such as land tenure, culture, history, attitudes, values, knowledge, learning, and access to information can be important social considerations.

3.5.1 Land Tenure

Land tenure is an issue with respect to decisions about liming. This arises because the effects of liming can be slow and it can be many years before the benefits of liming are fully realized. Where people have stable land tenure, they can make sensible long-term decisions about acid soil management, including liming, farming the least acid areas, or choosing acid-tolerant plants [78]. If land tenure is in doubt, the decision regarding lime use is largely irrelevant because of the uncertainty in recouping the cost of the investment.

3.5.2 History, Culture, Attitudes, and Values

In many European countries, the United States, and New Zealand there has been a long history and ingrained belief that liming acid soils is the “right thing to do” (see Refs. 79–81 for examples). The situation in Australia provides an interesting contrast because, until recently, it had limited liming culture. The use of lime was not part of its culture. This has had, and we suggest, will continue to have, a significant impact on how acid soils are considered in Australia and how the problem is to be resolved.

Consider for example the data in Table 4. Most scientists would agree that these data are consistent with the hypothesis that crop responses to liming are variable and cannot be predicted. The subsequent scientific activities flowing from such a conclusion are likely to follow one of two paths (Fig. 9). Some will progress with the logic that if lime responses are unpredictable, reflecting a complex subject, then the solution to soil acidity is to find alternatives to liming. In following this path, it is likely that they will be predisposed to find reasons not to lime and will review data accordingly. Those who choose the alternative path will set about finding out why lime responses are not predictable and develop the understanding, and hence techniques, to remedy this problem. They will be predisposed to regard liming as the solution to soil acidity. Neither path is right or wrong for both outcomes are potential solutions. The difficulty arises when one’s predisposition influences the objectivity with which the whole picture, including data relevant to both potential solutions, is viewed.

The broader cultural setting is likely to influence which path is chosen. This is illustrated by comparing the attributes of agriculture and agricultural research between New Zealand and Australia (Table 10). Given their intensive agriculture, favorable cost/product ratio, and an inherited prolime culture from Europe, it is not surprising that New Zealand has embraced the “lime is the solution” path. From early days, scientists have supported the use of lime and been encouraged to develop the appropriate diagnostic criteria and solutions. Only subsequently have
the New Zealand scientists concerned themselves with the other nonliming options such as managing the rate of acidification and plant tolerance to acidity.

In contrast, but with equally compelling logic, scientists in Victoria, Australia, have moved increasingly down the alternative path. For them, understanding the processes of ongoing acidification, in the hope of alleviating its impact, and the development of acid-tolerant plant material was the priority.
Problems arise when the path is set because any new issues, or interpretation of existing data, are examined through a mind set consistent with a cultural predisposition. An example of this is that one of the current authors (DCE) looks at the data in Table 4 and sees enormous opportunities, whereas the other (AMR) sees many insurmountable problems!

Other examples demonstrating the effect of cultural predisposition are highlighted in this chapter. The attitudinal difference between the soil chemist and the agronomist with respect to defining the optimal soil pH has now been resolved. Further time will be required before everyone will readily and without resistance distinguish between the soil lime requirement and the biological lime requirement.

Our reinterpretation of the data in Table 7 is a consequence of path-one thinking, as is our interpretation of Fig. 8. So too are the conclusions reached by Farina et al. [50] with respect to the economics of subsoiling (Fig. 6). Of course,

**TABLE 10** Case Study Comparison of the Physical, Economic, and Cultural Differences Between Pastoral Agriculture in New Zealand and Victoria, Australia

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Attribute</th>
<th>New Zealand</th>
<th>Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td>Rainfall (mm year(^{-1}))</td>
<td>600 to 2000</td>
<td>600 to 1000</td>
</tr>
<tr>
<td></td>
<td>Land value (AU$ ha(^{-1}))</td>
<td>1200 to 10000</td>
<td>1000 to 15000</td>
</tr>
<tr>
<td></td>
<td>Stocking rate (stock units ha(^{-1}))</td>
<td>5 to 30</td>
<td>5 to 25</td>
</tr>
<tr>
<td></td>
<td>Soil pHw</td>
<td>5.0 to 6.2</td>
<td>4.6 to 5.6</td>
</tr>
<tr>
<td></td>
<td>Response to lime (%)</td>
<td>0 to 10</td>
<td>0 to &gt;100</td>
</tr>
<tr>
<td>Economic</td>
<td>Gross margin (AU$ ha(^{-1}))</td>
<td>150 to 800</td>
<td>100 to 400</td>
</tr>
<tr>
<td></td>
<td>Lime cost (AU$ ha(^{-1}) on ground)</td>
<td>24 to 32</td>
<td>60 to 70</td>
</tr>
<tr>
<td></td>
<td>Cost/output ratio (lime cost/gross margin × 100)</td>
<td>4 to 20</td>
<td>16 to 64</td>
</tr>
<tr>
<td>Cultural</td>
<td>Historical farming practices</td>
<td>Conservative</td>
<td>Exploitive</td>
</tr>
<tr>
<td></td>
<td>Financial survival strategy</td>
<td>Intensification Increase production per unit area</td>
<td>Extensification Increase land holding</td>
</tr>
<tr>
<td></td>
<td>Sustainability strategy</td>
<td>High input–output maximize efficiencies</td>
<td>Low input minimize costs</td>
</tr>
</tbody>
</table>

\(^{a}\) Figures are generalized for the purpose of this comparison and should not be interpreted to indicate the financial viability of either system.
both approaches are required to solve the worldwide soil acidity problem, and to that end, a dispassionate, objective assessment of past lime research and future research needs is always required.

### 3.5.3 Knowledge, Learning, and Access to Information

Local knowledge is very important in making decisions about management of acid soils. An important farmer’s strategy has been to select, where possible, soils less constrained by acidity and to use acid-tolerant plant varieties [78]. This works where there is sufficient land available [62]. Learning is crucial in increasing farmers’ knowledge and ability to make informed choices about acid soils and liming. Extension is now developing from a reactive basis, whereby learning is a consequence of exposure to technology, to a program where education and understanding are the prime objective. Effective learning is achieved by doing rather than reading or listening to information. Community extension programs based on small numbers of farmers in their natural social groupings are useful for accelerated awareness and adoption of technology [82].

Better decision making is likely to result from increased access to information, provided the information is used in a discerning manner. Education and training are likely to result in an increased ability to filter appropriate information.

### 3.5.4 Off-Site Effects

In some situations, the broader off-site impacts and specifically the environmental and hence social impacts may also need to be considered. For example, if liming was practiced on a wide scale and for a long duration in pastoral agriculture in Victoria, Australia, it would be likely that large production increases would result. A commensurate increase in livestock would be required to harvest this production and make the investment economic. Nutrient inputs as fertilizer would also increase to balance the nutrient budget. A consequence could therefore be greater losses of nutrients, particularly N and P, to catchments and waterways.

Thus, improving the quality of the soil resource may adversely affect the quality of the water resource—is this desirable given its impact on the social resource? In such a case, it may be necessary, in the broader social interest, to forgo the value of the soil resource, even though the technology is available to do otherwise.

Such issues are intractable and highlight at the broadest level the theme of this chapter. Liming decisions at the biophysical level, while complex and difficult, can be made objectively provided the principles are clear and the biological data are available. However, such decisions may be different, and indeed irrelevant, within each cultural and social setting.
4 CONCLUSIONS

Much progress has been made in the last 50 years in understanding the nature of the soil–plant acidity complex and how lime can be used to ameliorate the adverse effects of soil acidity. It is now accepted that the old concepts of the ideal soil pH are no longer appropriate and the optimal soil pH and hence the soil lime requirement need to be defined in terms of the plant species and genotypes to be grown. It is also necessary to take into account the specific reason for poor plant performance. For these reasons, it is possible today to be more precise about the amount of lime required for optimal production in specific situations.

The processes that contribute to anthropogenic soil acidification highlight that all soils, not just those that are currently acid, have a requirement for lime or some other source of alkali. In addition, they emphasize the need to consider the fertility of the soil below the plow layer when the issue of soil acidity is considered.

It is possible to define a process for making decisions about lime use so that all components, the soil, plant, and the agricultural system involved, are considered. This highlights the weaknesses in the current body of knowledge. Specifically, the relationships between plant production and soil acidity—the production functions—need to be defined for the whole range of crops. Similarly, there is an urgent need for field-based measurements of soil buffer capacity and the duration of the liming effect on soil properties and plant production.

Together, this information is needed so that the long-term economics of liming can be examined in a systematic and objective manner. This will provide policy makers, planners, scientists, and advisers with a sound biological basis for confidently making lime recommendations. To achieve this, a change in attitude and culture is required, one that sees lime and liming as a solution to the soil acidity problem. However, decisions about lime use must also be considered within the broader social context. This arises because of the diversity in social, agricultural, economic, and environmental systems and constraints imposed on those who use and manage acid soils.

REFERENCES


35. AE Johnston, KWT Goulding, PR Poulton. Soil acidification during more than 100 years under permanent grassland and woodland at Rothamsted. Soil Use Manage 2:3–10, 1986.


58. MPW Farina, P Channon. A field comparison of lime requirement indices for maize.


Role of Organic Matter in Alleviating Soil Acidity

M. T. F. Wong
CSIRO Land and Water, Wembley, and The University of Western Australia, Nedlands, Western Australia, Australia

R. S. Swift
University of Queensland, Brisbane, Australia

1 INTRODUCTION

The principal adverse effects of acidity on soil fertility occur at soil pH values below 5.5 due to acid dissolution of aluminum (Al) and the onset of Al phytotoxicity to susceptible plants [1]. Aluminum phytotoxicity results in rapid inhibition of root growth due to impedance of both cell division and elongation [1]. This results in reduced volume of soil explored by the root system and direct interference with uptake of ions such as calcium and phosphate across the cell membrane of damaged roots [2]. These phytotoxic effects are unimportant in moderately acidic soils with pH values of 5.5 to 6.5 when the concentration of toxic forms of Al is normally negligible. Manganese toxicity and deficiencies of phosphorus, calcium, and magnesium are common in acidic soils. Soil nutrient deficiencies exacerbate the problem of inefficient nutrient uptake due to restricted root growth and root damage [3]. In drier environments, poor water use due to poor root development is considered to be another adverse effect of Al phytotoxicity.
The best management practice in these Al toxic soils is to treat acidity first because this promotes adequate root growth and function and allows nutrients and water to be taken up more effectively. Both exchangeable Al and Al saturation are used as indices of Al phytotoxicity because these values are dependent on the activity of Al in soil solution due to cation exchange processes. The severity of Al toxicity is directly dependent on the activity of inorganic Al species in the soil solution [4,5]. Organically bound Al species are less toxic [6–8]. Therefore the first objective of acid soil treatment is to decrease the activity of inorganic Al in soil solution. In most agricultural soils, the negative logarithm of the activity of monomeric inorganic Al (pAl) in soil solution is directly proportional to soil pH [9,10]. This simple linear relationship suggests that transient complexation of Al in soil solution by dissolved organic matter and by sulfate additions would not have a lasting impact on Al activity.

The main controlling factor is the soil pH. The direct way to decrease Al phytotoxicity (increase pAl) is therefore to increase soil pH. Lime has been used for thousands of years for this purpose. Large quantities of lime of the order of 1 to 10 tons per hectare are commonly required every few years for adequate crop performance. The slope of the pAl-pH relationship depends on the amount of protons required to dissolve Al from the solid phase. In the case of gibbsite and amorphous aluminum hydroxide, the slope is 3. The intercept is dependent on the solubility of the solid phase, which is greater for amorphous aluminum hydroxide than crystalline gibbsite. Both the slope and the intercept vary in soils; hence, another potential approach is to manage the soil and modify the linear relationship between soil pH and pAl to allow lower Al activity at any given pH value.

Numerous laboratory experiments that have been aimed specifically at measuring the effect of organic matter additions on soil acidity show increased soil pH, decreased Al saturation, and in some cases decreased Al solubility. Occasionally, the opposite happens and organic matter additions result in acidification. The findings of recent experiments have helped us to unravel the mechanisms involved in different types of organic matter. These mechanisms are reviewed here in order to explain the apparently conflicting observations. Our second aim is to show how the knowledge reviewed can be applied to treat soil acidity in farming systems. This approach is particularly important in low-input agroecosystems where high rates of lime cannot be used because of its high cost relative to the value of the farm products. It is also important where alternative, organically based sustainable agricultural practices are being sought.

2 MECHANISMS OF ORGANIC MATTER EFFECT ON SOIL pH

Organic materials that could potentially be used to ameliorate soil acidity include undecomposed plant materials, composts, manures, peats, and coal products. Ad-
ditions of undecomposed plant materials such as prunings to acid soils often result in increased soil pH, decreased Al saturation, and improved conditions for plant growth [11–14]. Similarly, addition of plant residue composts, urban waste compost, animal manures, and coal-derived organic products to acid soils have been shown to increase soil pH, decrease Al saturation, and improve conditions for plant growth [15–18]. The acid-ameliorating properties of farmyard manure and of undecomposed plant materials have been used to improve the yield of corn and beans on an acid Oxisol in Burundi [19]. Composts and manures are mostly derived from waste products that need to be disposed of in a sustainable way in order to avoid environmental pollution. Alkali-treated coal wastes from Victoria, Australia have a similar effect in increasing soil pH [20]. The recycling of these organic waste products for soil amelioration is a double benefit for both the environment and the economy provided that the waste materials are not contaminated with harmful impurities.

The principal mechanisms involved in increasing soil pH vary for organic materials, and a broad distinction can be made between undecomposed plant materials and composts, manures, peat, and coal products. Plant materials undergo decomposition in moist warm soils, and a high proportion of the proton consumption and corresponding increase in soil pH can be attributed to processes associated with decomposition. Composts, manures, peat, and coal products are more stable to decomposition than undecomposed plant materials and contain humic-type substances. The functional groups of these humic substances confer metal binding and pH buffering capacities, which are important in determining the pH of the treated soil. These two broad groups of organic substances are considered separately in order to illustrate the main mechanisms involved during acid amelioration.

2.1 pH Changes Induced by Additions of Composts, Manures, Peat, and Coal Products

Until recently, one of the main problems encountered when considering the use of composts, manures, peat, and coal products to treat acid soils on a routine basis was their compositional variability. This meant that their acid-ameliorating properties were uncertain and the use of these materials for ameliorating acid soils was risky because of insufficient knowledge of the mechanisms involved and unpredictable benefits. Several mechanisms have been postulated for explaining their effect on soil pH. These mechanisms include specific adsorption of organic anions on hydrous Fe and Al surfaces and the corresponding release of hydroxyl ions [16], proton consumption during reduction of metallic ions due to oxygen consumption during decomposition of composts and manures, and ammonification of labile organic N in composts and manures. The proposed liming effect of organic matter adsorption on hydrous Fe and Al surfaces is similar to that of sulfate ad-
sorption [21]. Adsorption of Al by organic matter sites and the subsequent dissolution of the inorganic phase to maintain the equilibrium Al activity in soil solution have also been postulated to increase soil pH [22].

These postulated mechanisms are possible, but their specific individual importance in contributing to pH change has not been evaluated. Composts, manures, peat, and coal products contain humic and fulvic substances with functional groups such as carboxyl groups that are able to consume or release protons according to their pKₐ values and the pH of the surrounding solution [23,24]. Progress in investigating the mechanism of acid amelioration experimentally involved the use of strong acid titration to pH 4.0 in order to determine the proton consumption capacity of samples of plant residue compost, urban waste compost, farmyard manure, and peat [22]. Subsequent aerobic incubation of these organic materials with moist samples of an Oxisol from Burundi, Ultisol from Cameroon, and Spodosol from Sumatra resulted in increased soil pH. The increase in soil pH was accompanied by a corresponding decreased exchangeable Al concentration, increased cation exchange capacity (CEC), and hence decreased Al saturation (Fig. 1). The pH of the incubated soils was linearly related to the proton consumption capacities (x, molₑ kg⁻¹) of the organic materials used. This suggests that the major mechanism for increased soil pH is proton exchange between the soil and added organic matter [22]. The regression

![Figure 1](image_url)

**Figure 1** Soil exchangeable aluminium following 2 weeks of incubation with 1.5% by weight of organic matter having different proton consumption capacities. (Redrawn from Ref. 22.)
equations for the pH of the incubated soils measured at 14 days of incubation were (Fig. 1)

- **Oxisol:** $\text{pH} = 4.51 + 0.29x, \quad r^2 = 0.999$ (1)
- **Ultisol:** $\text{pH} = 4.11 + 0.41x, \quad r^2 = 0.989$ (2)
- **Spodosol:** $\text{pH} = 4.06 + 0.61x, \quad r^2 = 0.991$ (3)

The constants of these linear regression equations were close to the pH values of the untreated soils. The slopes were indicative of the soil buffer capacity, the Oxisol being most strongly buffered and the Spodosol least buffered.

In order to test further that the increase in soil pH was due to the flow of protons from the soil to the organic matter sites, the pH of the incubated treated soil was predicted by plotting the buffer curves of both the organic material and the soil simultaneously (Fig. 2). The intersection of the two buffer curves predicted the incubated soil pH with good accuracy, confirming that the major process responsible for the increase in soil pH is simply proton exchange between the soil and added humified organic material. This work allows prediction of the treated soil pH that is valid across soils as well as providing an effective means of addressing the issue of variability in the composition of humified organic materials used in the treatment of soil acidity [22]. The treated soil pH can be predicted from

![Image](image_url)

**FIGURE 2**  Example of the initial pH and buffer characteristics of one organic material (urban waste compost) and the incubated soils. The pH buffering is shown for 1 kg soil and 15 g compost used during incubation. (Redrawn from Ref. 22.)
(1) the initial pH of soil and organic matter and (2) the buffer characteristics of soil and organic matter. The soil buffer characteristics should be relatively stable over a period of a few years and therefore, on a routine basis, only the soil and organic matter pH and the organic matter buffer characteristics are required. The increased soil pH leads to a corresponding increase in cation exchange capacity and decrease in Al saturation.

The implications of proton flow from the soil (lower pH) to the organic matter (higher pH) buffer systems as the main mechanism of acid amelioration is that, if the soil pH is higher than the organic matter pH, a decrease in soil pH will be measured due to flow of protons from lower pH (organic matter) to higher pH (soil). For example, application of sewage sludge compost with a pH value of 6.4 to a soil with a pH value of 7.7 resulted in decreased soil pH [25]. An important additional reason for a subsequent decrease in soil pH is further decomposition of less stable materials in the soil resulting in mineralization and nitrification of organic nitrogen. Using poultry litter and litter compost, Tyson and Cabrera [26] showed that there was an immediate increase in soil pH that could be attributed to proton flow from the soil. The soil pH increased further during incubation due to ammonification and peaked at 7 days of incubation. The soil pH then decreased to levels below those of the untreated control because of nitrification, which releases \( 2\text{H}^+ / \text{NH}_4^+ \), compared with ammonification, which consumes only \( 1\text{H}^+ / \text{NH}_4^+ \). The uncomposted litter had lower pH values than the composted litter due to larger amounts on nitrogen being nitrified. This nitrogen-led increase in soil pH is transient, and nitrification of organic N is expected to acidify the soil. The proton flows or alkalinity production associated with ammonification by deamination [Eq. (4)] and urea hydrolysis [Eq. 5] and with nitrification [Eq. (6)] are as follows:

\[
\begin{align*}
R-\text{CH} (\text{NH}_2)-\text{COOH} + 3\text{H}^+ + 2e^- & \rightarrow R-\text{CH}_2-\text{COOH} + \text{NH}_4^+ \quad (4) \\
\text{CO(NH}_2)_2 + 3\text{H}_2\text{O} & \rightarrow 2\text{NH}_4^+ + 2\text{OH}^- + \text{CO}_2 \quad (5) \\
\text{NH}_4^+ + 2\text{O}_2 & \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \quad (6)
\end{align*}
\]

The net longer term effect of addition of this type of more reactive nitrogen-rich organic manure is therefore expected to be determined by the balance between its proton consumption capacity and acid production by processes such as nitrification. Materials with high acid consumption capacities and low mineralizable nitrogen content would be more effective than materials with low acid consumption capacities and high nitrifiable nitrogen content.

### 2.2 Effect of Undecomposed Plant Materials on Soil pH

An initial increase in soil pH often occurs immediately upon addition of plant materials to acid soils [27]. This is a chemical process that is independent of biological activity [28]. Examination of the data presented by Tang and Yu [28] for five soils incubated with 10 plant materials shows that increased soil pH generally oc-
curred when the initial soil pH values were lower than those of the plant residues. Soils with pH values greater than those of the residues generally suffered a decrease in soil pH after treatment. This suggests that the mechanism postulated earlier for humified materials also applies for plant residues when microbial decomposition is absent. In these situations, the amount and direction of flow of protons between the soil and organic matter buffer systems dictate the direction of pH change; for very acid soils, an increased soil pH is normally observed. Following this immediate increase in soil pH, incubation of soil treated with plant residues under nonsterile conditions results in further increases in soil pH as a result of microbial activity.

The time course of soil pH during moist, warm incubation is varied and typically shows an increase to a maximum reached in 8 to 147 days, depending on the plant materials, amounts applied, and the soil properties [29,30]. This fluctuation gives rise to time-dependent relationships between the treated soil pH and plant residue composition [30]. These changes occur as a result of processes related to organic matter decomposition. Materials rich in organic nitrogen such as soybean leaves (29 g N/kg, C/N ~ 17) and barley grain (28 g N/kg, C/N ~ 18) result in a more pronounced peak than materials such as wheat straw with 5 g N/kg and C/N ~ 100 [29]. Comparisons of the pattern of pH change by plant materials with fully characterized model organic compounds suggest that ammonification of organic nitrogen in the plant residues is an important contributor to the pH increase to the peak values due to proton consumption [Eq. (4)]. The rate of ammonification of organic N depends on the C/N ratio of the plant materials and their lignin and polyphenol contents. The rate of ammonification is expected to be slow when the C/N ratio is >30. This ratio narrows during decomposition and results in increased ammonification rates. A subsequent decrease in soil pH occurs after ammonification due to nitrification of the ammonium ions and the release of 2 moles of protons per mole of ammonium. In the case of barley grain, which has a low base cation content of 256 mmolc kg⁻¹, nitrification causes the pH to fall to that of the untreated soil. The effect of ammonification is therefore transient [29]. This nitrogen-led pH fluctuation is less important with low-nitrogen residues [14,27].

An important and longer lasting cause of pH increase during incubation is microbial decarboxylation. This results in consumption of 1 mole of protons per mole of carboxyl [Eq. (7)]. The effect of decarboxylation on proton consumption can be illustrated with calcium oxalate [31]:

\[
\text{Ca}(	ext{COO})_2 + \frac{1}{2} \text{O}_2 + 2\text{H}^+ = 2\text{CO}_2 + \text{H}_2\text{O} + \text{Ca}^{2+} \tag{7}
\]

A good correlation is therefore obtained between the soil pH increase and the amount of carbon dioxide evolved during incubation of soil treated with organic anions [32]. According to Eq. (7), the amount of alkalinity associated with calcium mineralized from the simple organic molecules has the same liming effect as the amount of alkalinity associated with calcium found in lime; in each case
$2H^+/Ca^{2+}$ are consumed during acid neutralization. The reaction is, however, slower than that with lime because decomposition is involved. The neutralization process is quicker with materials with a higher nitrogen content, which increases the rate of decomposition [29]. With plant materials, calcium is present with additional base cations such as magnesium and potassium. The sum of charge carried on these base cations is closely related to the ability of undecomposed plant materials to neutralize soil acidity [29,30]. This cation charge is related to ash alkalinity of the plant material measured by titration of its ash [33]. For example, incubation of an Oxisol and an Ultisol with prunings from seven agroforestry tree species with base cation content ($b$, cmol$_c$ kg$^{-1}$) increased soil pH measured at 14 days [30]:

\[
\begin{align*}
\text{Oxisol} & \quad \text{pH} = 5.61 - 1.58b + 0.77b^2, \quad r^2 = 1.00 \\
\text{Ultisol} & \quad \text{pH} = 4.23 - 0.74b + 0.62b^2, \quad r^2 = 0.95
\end{align*}
\]

The pattern of soil pH during incubation with plant materials is due to a combination of the transient effect of ammonification, the reversal of the ammonification effect by nitrification, and the release of alkalinity by the decarboxylation process. These processes are governed by the chemical composition of the plant materials. In addition to the chemical composition, the time course of soil pH during incubation is dependent on the soil type (Fig. 3). The pH of the treated Ultisol measured at 42 days was higher for all treatments than that measured at 14 days.

![Figure 3](image-url)

**Figure 3** Effect of total base cation content of tree pruning on soil pH in an Oxisol and an Ultisol measured at (A) 14, (B) 42, and (C) 98 days of incubation. (Redrawn from Ref. 30.)
days, but was the same as that measured at 98 days. In this soil, the total base cation content remained a good predictor of the pH of the treated soil throughout the 98-day incubation period. In contrast, the pH reverted to lower values after a 14-day incubation in the Oxisol. Comparison of the effects of lime with those of the base cations present in the plant materials showed that with the Oxisol, the base cations were as effective as lime when measured at 14 days. A similar relationship was obtained for the Ultisol at 42 days, suggesting that in both cases the base cations were as effective as lime in acid amelioration. This is in accord with measurements made for the decarboxylation of simple nitrogen-free organic molecules. In the case of the plant materials, the presence of nitrogen meant that the measured pH values deviated from those achieved by using lime (Fig. 4). The Oxisol had a higher organic carbon content (45 g C/kg) than the Ultisol (26 g C/kg); this is expected to lead to more rapid decomposition of the pruning materials because both soils had similar clay contents [34]. It is feasible that further nitrification may decrease the pH of the Oxisol below that of the untreated control after 98 days. In another soil, the liming effect persisted as long as 574 days [29]. The duration of acid amelioration is therefore long enough to provide a window for crop growth in soils that are normally Al toxic. The decarboxylation process results in a change in the buffering properties of the soil from more strongly acidic to weaker acidic functional groups, resulting in stronger retention of protons [27].

The current trend is to rank the acid amelioration value of plant materials according to their total base cation content because this property is related to their longer term effect following the transient effect of ammonification. Total base cation content can be estimated from published tabulations of leaf nutrient levels, e.g., Drechsel and Zech (35) for broad-leaved tropical trees. Because the total base cation contents are deemed to have the same amount of alkalinity as the cation

![Figure 4](image-url)

**Figure 4** Comparison of the measured and expected soil pH in an Oxisol and an Ultisol after (A) 14, (B) 42, and (C) 98 days of incubation assuming that the net acid-neutralizing capacity of each pruning addition is equal to its base cation charge. The 1:1 line is given for reference. (Redrawn from Ref. 30.)
content of lime, relatively large additions are required because of the low base cation content compared with lime. This ranking is a first step because the temporal patterns of acid amelioration achieved by different plant materials are different and field experiments showed that the ranking of plant materials measured in the laboratory did not match that measured in the field [36]. Additional processes, such as leaching and crop uptake of nutrients, further complicated the prediction of acid amelioration.

3 DECREASING Al SOLUBILITY BY MODIFYING THE RELATIONSHIP BETWEEN PH AND PAL

The activity of Al$^{3+}$ in soil solution of mineral soils is often described by using the solubility of an aluminum hydroxide phase such as natural gibbsite as follows:

\[
\text{Al(OH)}_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O} \tag{10}
\]

\[
\frac{[\text{Al}^{3+}]}{[\text{H}^+]^3} = \text{constant} \tag{11}
\]

\[
\log \text{Al} + 3\text{pH} = \log k \tag{12}
\]

The value of \(\log k\) at 298 K varies from 8.11 to 8.77 depending on the solubility of the mineral phase in soil. The slope of the relationship between \(\log \text{Al}\) and pH is 3. This approach often overestimates the activity measured at pH <5.0. In addition, the cubic relationship between pH and pAl is often not observed. The undersaturation has sometimes been attributed to kinetic constraints to mineral dissolution. Although this may occur in some soils, there is increasing evidence that at low pH values, organic matter Al complexes control the activity of Al in soil solution [37–41]. This allows acid soils with high organic matter content or soils amended with organic matter to have low soil solution Al concentrations and to grow good crops under conditions that would normally exhibit Al toxicity.

The relationship between pAl and pH is also normally linear at the natural acid soil pH values when organic matter Al complexes control the activity of Al in the soil solution. The slope is often <3. In some North American soils, the slope could be predicted from its linear relationship with the bound Al ratio. This ratio is determined by extracting organically bound Al with CuCl$_2$ and is defined as the equivalents of Cu-extractable Al per unit organic matter divided by the equivalents of carboxyl groups per unit organic matter [37]. The intercept is inversely proportional to the bound Al ratio. As the bound Al ratio decreases, Al solubility also decreases provided that soil pH <5.0 because the organic-Al and Al(OH)$_3$ solubility lines intersect at about this pH value [37]. Further work on a larger range of O horizon samples of Spodosols, Alfisols, Ultisols, and Inceptisols showed that average values of slope and intercept based on the bound Al ratio could be used [39]. The equilibrium Al activity was reached within a 48-hour period. It is un-
likely that the observed undersaturation was due to kinetic restriction of dissolution of the Al(OH)₃ phase as is sometimes postulated.

Further work by Mulder and Stein [42] and Wong and Swift [43] suggests that the often-measured undersaturation is due to the control of Al activity by organic matter–Al complexes rather than slow dissolution of the mineral phase. Organic matter–Al complexes have also been found to control Al activity in the mineral soil layer and account for the apparent undersaturation with respect to Al(OH)₃ [38,40,42,43]. A decrease in Al solubility was observed with decreases in the ratio of organically bound Al to total soil organic carbon. The bound Al ratio also controls the nature of the relationship between pH and pAl, which becomes increasingly curvilinear as the ratio increases. Linear regression is simple, easy to use, and adequate in many situations, but it appears to be unsatisfactory at a bound Al ratio >0.7 and outside the pH range of 3–5 because deviation from linearity increases at very low pH values and at pH >5 the gibbsite equilibrium appears adequate in modeling the soil solution Al activity. This nonlinear behavior can be predicted with more generally applicable mechanistic chemical equilibrium models such as Windermere humic aqueous model (WHAM), which considers specific and nonspecific ion binding by humic substances [41].

Increasing total soil carbon with organic matter additions increases the carboxyl content and CEC. This can also decrease the bound Al ratio. Artificial addition of humified organic matter to acid subsoil has been shown to decrease the concentration of Al at any pH values compared with the untreated soil [44]. This decrease in Al concentration was accentuated with increasing additions of organic matter. The lowered aluminum concentration allowed barley to grow better in organic matter–treated acid soil than the untreated control at the same pH values [44]. The activity of Al in soil sampled from the A horizon of an Oxisol from Burundi and an Ultisol from Cameroon was undersaturated with respect to the solubility of natural gibbsite. Wong and Swift [43] postulated that the undersaturation was due to the control of soil solution Al by organic matter–Al complexes and showed that Al solubility could be decreased further in these mineral soils by additions of organic matter. The organic matter treatment lowered the solubility of Al, giving rise to lower Al activity in solution at any given pH in the range of 3.3 to 4.8. The treatment did not change the slope of the solubility lines measured at 12 and 28 days of incubation. In the Oxisol only, the slope increased from 2.16 to 2.74 at 35 days of incubation. The treatment continued to have no effect on the slope measured at 35 days of incubation for the Ultisol. These A-horizon samples therefore appear to behave differently from the O-horizon soil samples used by Cronan et al. [37]. The decreased Al solubility with humic acid treatment led to a corresponding decrease in Al saturation [43]. Soil incubation with plant residues appears to have a similar effect, and over a range of pH values the concentrations of monomeric Al found in the residue-treated samples were generally lower than those of the samples treated with lime [33]. This effect would decrease the soil pH
at which Al phytotoxicity occurred. The effect of organic matter on Al solubility could explain earlier observations that at the same pH values, higher soil organic matter content corresponded to lower exchangeable Al concentrations [44,45]. The opposite—an increase in Al solubility at a given pH—is observed when lime is used because of the formation of more soluble freshly precipitated Al hydroxide [10].

Increased uptake of Al is often observed as the soil pH value is increased from 5.5 to the neutral value. Farina et al. [46] observed a corresponding decrease in crop yield in an Oxisol and an Ultisol containing 6.6 and 3.2% organic matter. This effect is less pronounced in subsoils than in the corresponding topsoil samples [47] but is more pronounced in soil that has been treated with organic matter [44]. This increased uptake of Al at the near-neutral soil pH may be due to increased solubility of Al–organic matter complexes in that pH range [48]. The solubility line for organically bound Al crosses that of soil Al(OH)₃ at about pH 5.5. The soil solution will maintain oversaturation with respect to natural gibbsite above this pH value until amorphous Al(OH)₃ is precipitated [39]. The presence of organic matter in soil solution would interfere with this precipitation and favor oversaturation by Al [49].

4 AMELIORATION OF SUBSOIL ACIDITY

Subsoil acidity occurs below the depth at which lime can be incorporated by “normal” cultivation methods so that amelioration relies on the slow movement of lime or the use of more mobile amendments such as gypsum and soluble organic matter. Naturally occurring and agriculturally generated subsoil acidity limits root growth and hence nutrient and water uptake by susceptible crops at depth and is a threat to the sustainability of agriculture in many regions throughout the world [50–52]. The use of lime to treat subsurface acidity has met with varied success because of its low solubility in acidic to neutral soil conditions, giving rise to variable mobility of lime alkalinity down the soil profile [53]. Downward movement of lime is a function of soil type, rate of addition, soil pH, and rainfall and is feasible in sandy soils [52], whereas in more heavily textured soils, physical deep incorporation of lime into the soil profile is needed [50]. This practice is costly and may not be economic in many places. Gypsum and phosphogypsum are more mobile and are often effective in treating subsoil acidity. The effectiveness of gysiferous materials in increasing subsoil pH is variable because the self-liming effect of gypsum occurs as a result of ligand exchange of sulfate anion for hydroxyl anion on hydrous Fe and Al surfaces [21]. Ligand exchangeable hydroxyl anions must be present on the relevant variable charge soil surfaces for self-liming to occur. Some crops such as lupins are sensitive to gypsum application, and this limits its use for this crop in Western Australia. In the absence of ligand exchange, gypsum may still provide some benefits such as overcoming calcium deficiency,
increasing the Ca/Al ratio, and increasing the ionic strength of the soil solution and hence decreasing the relative activity of Al.

The variable success of lime and gypseriferous materials in controlling subsoil acidity has led to research on the use of soluble organic materials to treat the problem. One of the first products used was calcium fulvate obtained from the wet oxidation of coal and neutralization of the water-soluble product with calcium hydroxide. In a column experiment, calcium fulvate was consistently found to increase soil pH to a depth of 100 cm after application of two pore volumes of water in soils containing 6, 20, and 36% clay, whereas application of the same amounts of calcium as gypsum decreased subsoil pH and lime (applied as calcium hydroxide or as calcium carbonate) had little effect below the depth of application [18]. The sulfate-induced self-liming effect of gypsum was not apparent in these soil samples, and the salt effect resulted in lower pH values.

Further soil column experiments using calcium fulvate and a less soluble oxidized calcium-saturated coal product again showed the inability of lime to treat the soil below the depth of incorporation, whereas the coal products were able to ameliorate acidity at depth in a red podzol by increasing soil pH and decreasing exchangeable Al [54]. Similar work on a repacked 50-cm-long column of a Ultisol (pH 4.4) showed that only 2% of added lime moved past the 15-cm depth with 300 mm leaching with water. Lime had no effect on exchangeable aluminium below 10-cm depth. In contrast, 35–75% of calcium fulvate derived from chicken manure, cowpea green manure, and sewage sludge moved beyond this depth. The calcium fulvate derived from sewage sludge decreased Al down to the 45-cm soil depth. The other calcium fulvates were less effective [55]. Calcium fulvate derived from a pasture soil and calcium citrate were also found to be effective in ameliorating the subsoil by complexing and removing Al from the soil column. Calcium chloride and phosphogypsum were unable to displace Al from the column [56]. Although these examples show the effectiveness of organic materials in ameliorating subsoil acidity and aluminum toxicity under laboratory conditions, little work has been done in assessing their potential in the field from the point of view of waste management, economics, environmental impact, and crop yield.

5 AMELIORATION OF ALUMINUM PHYTOTOXICITY BY ROOT EXUDATION OF ORGANIC MATTER

Root apices (terminal 3–5 mm of roots) are the primary site of Al-induced inhibition of root growth, and many plants have evolved resistance to Al phytotoxicity by releasing simple low-molecular-weight aliphatic organic acids at the root apex to complex soluble toxic Al. The organic acids released include citrate and malate, which react strongly with Al and convert it to less toxic organically bound forms. The organically bound Al is less readily taken up by root apices and is hence excluded from the plant. Cultivars differ considerably in their ability to detoxify Al
in this way and give rise to genetic-based variability in resistance to Al. This mechanism of Al detoxification has been reported in tolerant cultivars of many crops including barley, buckwheat, canola, lupins, maize, oats, snapbeans, soybeans, and wheat. Resistance to Al and root growth in soybean cultivars is related to the rate of root exudation of citrate, which is induced specifically by exposure to Al. Other metals and P deficiency failed to induce citrate exudation. Plants take up the Al-citrate complex poorly, and this allows root growth to increase while Al uptake decreases due to Al exclusion from the root apex [57].

Maize exudes malate in addition to citrate. When the roots of tolerant and sensitive maize plants were grown in nutrient solutions containing a series of Al concentrations, dose-dependent citrate and malate exudation was observed in the tolerant but not the sensitive roots. The rate of citrate exudation was two to four times that observed for malate [58]. Exudation of malate is more important than citrate for conferring Al resistance in wheat. Tolerant genotypes release 5 to 10 times more malate than a near-isogenic but sensitive genotype. Malic acid release is detected as quickly as 15 minutes after exposure to 200 μM Al and is stimulated with as little as 10 μM Al. The amount released increased linearly over 24 hours and was dependent on the external Al concentration. Only Al triggered the release of malic acid at root apices. Other metals and P deficiency were unable to elicit this response [59]. Other studies of wheat showed that roots of tolerant cultivars release 100–120% more malate on exposure to Al than sensitive cultivars, where exudation of malate is decreased [60]. Half-maximal efflux of malate from root apices of Al-tolerant wheat seedlings occurred at 30 M Al in 0.2 mM CaCl₂, pH 4.2. Maximum efflux of 2.0 nmol apex⁻¹ hr⁻¹ occurred with concentrations greater than 100 μM Al [61]. A study using 36 genotypes of wheat showed a significant correlation between relative tolerance to Al (estimated from the length of Al-exposed roots expressed as a percentage of the root length achieved under Al-free conditions) and the amount of malate released from root apices under standard Al treatment [62]. Plant breeding and genetic engineering offer an additional means of matching crops to Al toxic soils, but this may reveal other plant nutritional and environmental problems.

The work on Al exclusion by organic matter complexation at root apices was done in culture solutions. The strong relationship between pH and pAl in many acid soils suggests that the chelating effect of root exudation of soluble organic acids on Al activity surrounding the root tip would be transient because the pressure would be for the equilibrium Al activity to be reestablished quickly. Simple organic compounds such as malate undergo rapid microbial decomposition in soil. The half-life in soil is about 1.7 hours irrespective of the soil pH between pH 4.3 and 5.0 [63]. Decarboxylation is a major process of organic matter decomposition under aerobic conditions. It appears that malate efflux from apices of Al-tolerant wheat roots occurs as potassium malate [61]. Decarboxylation of unprotonated malate and citrate is expected to increase the pH of the rhizosphere and
provide the root tip with an additional mechanism for Al exclusion by precipitation. As root growth occurs, the anticipated loss of Al detoxification in the original zone of the root tip would not be important because the rest of the root is much less sensitive to Al toxicity. Continuous production and exudation of Al-binding organic acids are required at the root apex in order to escape the effects of Al toxicity as new soil volumes are explored.

6 NUTRITIONAL EFFECT OF ORGANIC MATTER ADDITIONS

Calcium and magnesium deficiency is common in acid soils and exacerbates the problem of Al phytotoxicity. Provision of these base cations alleviates to some extent the effect of Al toxicity on roots (64). It is suggested that the mechanism of toxicity alleviation is reduction of Al accumulation in root apices (65). The calcium and magnesium content of organic matter is expected to alleviate further the effect of Al phytotoxicity. Phosphorus (P) deficiency is also often associated with Al phytotoxicity. Plant residues and manures contain significant amounts of inorganic and organic P, and addition of organic amendments with C/P <100 alleviates P deficiency. The release of inorganic P contributes to both the soil solution and adsorbed pools. Adsorption of P derived from organic matter will decrease the sorption of a further addition of fertilizer P by occupying the more active sorption sites first. As well as direct addition of P, organic matter ameliorates P deficiency by reacting with soil and fertilizer. Organic matter addition decreases the activity of Al and Fe in soil solution by (1) increasing soil pH and (2) forming strong complexes with these metallic ions. The lowered Al and Fe activities decrease the precipitation of P with these metallic ions and decrease the amount made unavailable to plants. Low-molecular-weight aliphatic organic anions such as citrate, tartrate, and malate released into the rhizosphere by some plants have a similar effect in decreasing Al and Fe activities and increasing P availability and uptake by roots. These organic anions are also added as part of the organic residue or are formed as a result of residue decomposition. The organic Al affinities or stability constants are in the order citrate > tartrate > malate (7). The functional groups involved in metal complexation are COOH and OH. These functional groups are also prevalent in humic and fulvic acids. Complexation of Al and Fe by these groups will favor the dissolution of P already precipitated with a range of Al and Fe minerals.

The concentration of P in soil solution is mainly regulated by specific adsorption–desorption reactions. Specific adsorption occurs when solution P anion replaces ligands such as OH\(^-\) ions and/or OH\(_2\) molecules from hydrous Fe or Al surfaces to form surface complexes. The presence of large hydrous Fe and Al surface areas in highly weathered acid soils such as Oxisols and Ultisols and in volcanic soils with andic properties is the main reason for strong P adsorption and high P requirement in these soils. These surfaces have a high zero point of charge...
and may be positively charged in acidic conditions. The positive charge would also retain P anion by nonspecific coulombic attraction. Increased soil pH and increased negative charge following organic matter addition decrease P adsorption by providing an unfavorable negatively charged environment for adsorption.

In some soil types, specific adsorption of P is decreased by competition for P adsorption sites by organic anions. Simple organic anions such as citrate and oxalate that are released in the rhizosphere are very effective in decreasing the specific adsorption of phosphate. Malate is moderately effective. This effect is in addition to decreasing Al and Fe activities. The effectiveness of these anions in decreasing P adsorption is determined by the relative stabilities of the Fe (or Al)–organic anion complex and the Fe (or Al)–phosphate complex. Polygalacturionate, which is a pectic substance found in mucigel surrounding root surfaces, is very effective in this regard [66]. Humic and fulvic acids compete strongly with P for adsorption sites on goethite, gibbsite, and tropical soils at acidic pH values. These acids decrease P adsorption further by generating an unfavorable negatively charge electric field around the adsorbed humic and fulvic acid molecules [67]. The effect of organic matter on P sorption appears dependent on the size of the molecule. Dissolved organic matter derived from green manure (molecular weight 710 to 850) was found to inhibit P sorption compared with DOC derived from animal manure (molecular weight 2000 to 2800), which had no effect on P sorption [68]. Addition of humic and fulvic acids does not always decrease P sorption in soils. In volcanic soils, the new humic acid–Al complex formed by adsorption of humic acid acts as a new source of P sorption sites [69]. Hue [16] showed that the efficiency of fertilizer P was improved when applied with green or animal manures. In the case of rock phosphate, mixing with animal manures, composts, or plant residues improves dissolution by removing and chelating calcium from the fertilizer (69). The added benefit of using organic matter to alleviate Al phytotoxicity is that plant nutrients are recycled and soil organic matter levels and physical and chemical conditions are improved.

7 APPLICATION IN MANAGING ACIDITY IN FARMING SYSTEMS

Addition of undecomposed plant residues, composts, and manures increases soil pH by transferring alkalinity from one place to another. The pH benefit of organic matter addition is at the expense of the place of origin of this alkalinity. Most plants using nitrate as their main source of nitrogen increase the rhizosphere pH due to excess anion uptake over cation uptake and the release of bicarbonate or hydroxyl ions to maintain electrical neutrality. These plants are poor in taking up and transferring alkalinity. Leguminous plants relying mainly on nitrogen fixation take up excess base cations over anion and release protons in the rhizosphere to maintain electrical neutrality. Similar excess cation uptake and rhizosphere acidification oc-
cur with plants fed with ammonium ions as the main source of nitrogen. The harvest and use of plant materials result in a net transfer of alkalinity from the site of rhizosphere acidification. Deep-rooted perennial leguminous plant species such as lucerne and agroforestry tree species can be used in farming systems to redistribute alkalinity from more alkaline areas to where acid amelioration is needed. The spatial distribution of the source of alkalinity varies in different landscapes. The source of alkalinity may be vertically below the acid soil layer and may occur in the form of basic saprolite or alkaline soils within the root zone of the deep-rooted plants. In other cases, the entire root zone may be acid, but spatial variation in soil pH may occur at the landscape scale as a result of pedogenic processes.

A common example that occurs on the ancient drainage landscape in Western Australia [70] is calcium carbonate accumulation in the lower parts of the landscape, whereas soils in the upper parts are acidic. Two examples of agroforestry systems in South Sumatra for the redistribution of alkalinity to deal with their different spatial distributions in the landscape have been described [71]. First, a hedgerow intercropping system with shallow-rooted crops grown between alleys of trees was used to redistribute alkalinity from lower parts of the profile to the topsoil. Second, pure stands of trees were grown and prunings cut, transported, and applied on the acid soil to demonstrate the transfer of base from the production to the mulch plots. Both systems were effective in treating soil acidity, and the system recommended takes into account the location of source of alkalinity. Prunings from the *Gmelina* tree had a high base cation content but were unsuitable for hedgerow intercropping because it outcompeted the crops [71]. This tree species should perform well in a lateral base transfer and mulch system that can also incorporate animals and the recycling of manure. Amelioration of Al toxicity is therefore only one of the terms in an overall tree–soil–crop interaction and other criteria should be assessed simultaneously.

8 CONCLUSIONS

Laboratory work has shown that the major effect of a wide range of organic materials on soil acidity is increased soil pH. There are additional benefits in lowering the solubility of soil Al so that lower activities are obtained at a given soil pH. This lowering of Al activity can also be achieved by direct Al complexation by organic acids released by root apices of Al-tolerant plant species and varieties and released by added organic materials. The pH effect of organic matter is expected to extend to the subsoil better than liming materials because of higher solubility of simple low-molecular-weight organic acids and of fulvic acids. The pH effect of organic matter additions can be predicted under laboratory conditions. Increases in pH due to ammonification are short lived because of subsequent acidification through nitrification. The effect of decarboxylation and proton flows between pH buffer systems is long lasting.
This knowledge can be used to develop farming systems that conserve and transfer alkalinity to more acid surfaces in the landscape. There is little evidence so far that an integrated approach is being taken to manage acidity in low-input farming systems to take account of possible significant fluxes of alkalinity within and from the farms. There is an urgent need to develop such an approach, which will enhance the environment by conservation and by providing a valuable use for a wide range of organic waste materials. Development of a research and demonstration village-scale model to test the sustainability of such a system under real-life conditions would be the first step toward such an integrated approach. An additional benefit of organic matter use is the recycling of plant nutrients and increased nutrient availability due to both direct addition and reactions with soils and fertilizers that increase nutrient availability, especially phosphate availability.

REFERENCES

Organic Matter in Alleviating Soil Acidity


13

Fertility Management of Tropical Acid Soils for Sustainable Crop Production

Nand K. Fageria
National Rice and Bean Research Center of EMBRAPA, Santo Antônio de Goias, Brazil

Virupax C. Baligar
Alternate Crops and Systems Laboratory, Beltsville Agricultural Research Center, USDA-ARS, Beltsville, Maryland

1 INTRODUCTION

Tropical regions have the largest land area available for agricultural production to meet growing demand for food by the rapidly increasing world population. Tropical agriculture, however, is faced with a serious challenge of feeding about 70% of the world’s inhabitants and meeting other basic necessities of life for 75 to 80% of the population of the region that depends on farming. A significant portion of the population in tropical countries suffers from malnutrition. In addition to economic issues, intensification and extension of agriculture to marginal lands have created severe ecological problems (e.g., deforestation, soil degradation, pollution of water and the natural environment, and increased greenhouse gas emissions). In these situations, adopting sound practical measures to maintain and/or improve the nutrient-supplying capacity of tropical soils is the key factor to improving and/or sustaining the long-term crop production.
There is a need to define soil fertility and crop sustainability in tropical soils before discussing the fertility management practices. Soil fertility is the quality of a soil that enables it to provide nutrients in adequate amounts and in proper balance for the growth of specified plants or crops [1]. Soil fertility is sometimes confused with soil productivity and soil quality. These terms are, however, distinct. Soil productivity is the capacity of a soil to produce a certain yield of crops or other plants with a specified system of management. In contrast, soil quality is the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health [1].

Sustainable agriculture is the management and utilization of the agricultural ecosystem in a way that maintains its biological diversity, productivity, regeneration capacity, vitality, and ability to function so that it can fulfill, today and in the future, significant ecological, economic, and social functions at the local, national, and global level without adverse effects on the other ecosystems [2]. Tropical soils may be defined as all soils that occur in the geographic tropics, that is, in the region of the earth lying between the tropic of Cancer and the tropic of Capricorn, also known as the torrid zone [3]. There are diverse types of soils in the tropical regions. However, acidic, low-fertility soils meeting the stereotypic concept of tropical soils are mainly classified as Oxisols and Ultisols, covering about 43% of the tropics, including large areas in South America and central Africa [4].

Low natural and/or declining soil fertility is the main constraint on improving the yield of annual crops on most tropical acid soils. Sub-Saharan Africa is a region facing massive problems of food security due to decreasing per-capita food production. A team of international researchers has identified declining soil fertility as the fundamental cause of declining productivity in Africa [5].

Most of the central part of Brazil is occupied by a tropical savanna, locally known as the “cerrado,” which covers about 205 million ha or 23% of the national territory. Most soils in this region are highly weathered Oxisols (46%), Ultisols (15%), and Entisols (15%), with low natural soil fertility, high aluminum saturation, and high P fixation capacity (Table 1). In addition to cerrado, there are about 30 million ha of lowlands, known locally as “varzea” in Brazil. At present, about 1.5 million ha of these lowlands are under cultivation. Generally, varzea soils have good initial soil fertility, but within 2 to 3 years of cultivation, fertility declines [6].

Farming systems need to be developed with improved soil management technology to bring these areas under successful crop production. Supply of sufficient amounts of nutrients is one of the key factors in improving crop yields and maintaining sustainable agricultural production on these lowlands. Soil fertility management for sustainable crop production represents a resource-efficient option in maintaining adequate nutrient levels. This is an important aspect in sustaining our soils and consequently the society. The objective of this chapter is to suggest appropriate management strategies for improving the nutrient status of tropical acid soils for sustainable crop production.
The current knowledge of the soils in the tropics clearly indicates that there is considerable diversity of soils, and the immediate need is to manage this diversity in the context of sustainable agriculture. Liming and adequate rates of fertilizer application are the most effective management strategies to overcome acidity and soil fertility constraints to crop production in the highly weathered soils of the tropics. However, use of gypsum; control of soil erosion; maintenance of organic matter content; use of nutrient-efficient or toxicity-tolerant crop species or cultivars within species; adoption of appropriate crop rotation; creation of irrigation facilities; control of insects, diseases, and weeds, control of allelopathy; and favorable socioeconomic factors for the farmers are other complementary practices that can be adopted in fertility management of these soils for sustainable crop production. Therefore, an adequate soil fertility management program requires integration of numerous technological but also socioeconomic factors.

2.1 Liming

Soil acidity, either natural or developed by human activities, has serious negative effects on the sustainability of crop production in various parts of the world. The predominant constraint resulting from increasing soil acidity is a severe chemical imbalance caused by toxic levels of Al, Mn, and H ions coupled with a parallel critical deficiency in available N, P, K, Ca, Mg, Mo, and sometimes Zn. Ion toxicities and Ca deficiency are not necessarily mutually exclusive injuries. The micro- and macronutrient imbalances result in impaired physiological, biochemical, and/or metabolic processes that affect crop growth detrimentally [7].

<table>
<thead>
<tr>
<th>pH (H₂O)</th>
<th>Ca (mmol dm⁻³)</th>
<th>Mg (mmol dm⁻³)</th>
<th>Al (mmol dm⁻³)</th>
<th>P (mg dm⁻³)</th>
<th>K (mg dm⁻³)</th>
<th>Cu (mg dm⁻³)</th>
<th>Zn (mg dm⁻³)</th>
<th>Fe (mg dm⁻³)</th>
<th>Mn (mg dm⁻³)</th>
<th>OM (g dm⁻³)</th>
<th>Base saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>6.4</td>
<td>5.8</td>
<td>6.4</td>
<td>1.2</td>
<td>47.2</td>
<td>1.3</td>
<td>1.0</td>
<td>116</td>
<td>14</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>5.3</td>
<td>49</td>
<td>31</td>
<td>13</td>
<td>16</td>
<td>92</td>
<td>2.2</td>
<td>2.4</td>
<td>303</td>
<td>59</td>
<td>31</td>
<td>50</td>
</tr>
</tbody>
</table>

* The data are average values of 200 soil samples collected from six states covering cerrado region.
* The data are average values of 55 soil samples collected from eight states covering varzea soils.

Source: Adapted from Ref. 77.
FIGURE 1  Relationship between lime applied and pH of an Oxisol of central Brazil. (Adapted from Ref. 47.)

FIGURE 2  Relationship between lime applied and extractable Ca and Al concentrations in the lowland acid soil of central Brazil. (Adapted from Ref. 81.)
Improper management of agricultural systems result in the inefficient use or loss of basic cations through excessive removal in biomass and leaching losses [8,9]. Liming is the most dominant and most effective practice to replenish the soil cation pool [10]. Liming increases soil pH (Fig. 1), Ca concentration (Fig. 2), cation exchange capacity (Fig. 3), and base saturation (Fig. 4), simultaneously.

**Figure 3** Relationship between lime applied and effective cation exchange capacity of acid lowland soil of central Brazil. (Adapted from Ref. 81.)

**Figure 4** Relationship between lime applied and base saturation of an Oxisol of central Brazil. (Adapted from Ref. 47.)
lowering the Al concentration (Fig. 2). All these chemical changes, provided they are within a favorable range, improve grain yields and crop sustainability. Figure 5 shows the response of soybean (*Glycine max* L. Merr.), common bean (*Phaseolus vulgaris* L.), and corn (*Zea mays* L.) to liming on an Oxisol of central Brazil. A significant quadratic response was obtained with the three crops. Based on regression equations, the maximum yield of soybean was achieved at 14 t lime ha\(^{-1}\). In the case of common bean and corn, the maximum grain yields were obtained at 11 and 9 t lime ha\(^{-1}\), respectively. Therefore, among these three crops soybean was most sensitive to soil acidity and corn was least sensitive. Overliming, however, may cause deficiency of some micronutrients, such as Mn, Zn, Cu, B, and Fe, if soils are relatively poor in these elements. Iron deficiency in upland rice (*Oryza sativa* L.) grown in Oxisols of Brazil has been reported [11]. The iron deficiency in these soils is caused by liming. Due to improved technologies, farmers use lime at an adequate level to raise the soil pH to about 6 and 6.5 for crops such as soybean and common bean. However, when rice is planted after these crops in rotation, it shows Fe deficiency symptoms. This deficiency is related to Fe uptake and utilization by rice plants and not to deficiency of this nutrient in the soil. Iron
in the limed soils precipitated according to following reaction:

\[ \text{Fe}^{3+} + 3\text{OH}^- = 	ext{Fe(OH)}_3 \text{ (precipitated)} \]

Lindsay [12] reported that an increase of one unit of soil pH above pH 4 decreases the solubility of iron by a factor of about 1000. Concentrations of other elements such as Mn, Zn, and Cu also decreased with increasing pH; however, this decrease was about 10 times lower than that of iron [12].

Base saturation, aluminum saturation, and pH are generally used as indices of soil acidity in making decisions on improving crop yields on acid soils by liming. Base saturation can be calculated by the following formula:

\[ \text{Base saturation} = \frac{\sum \text{exchangeable Ca, Mg, K, Na}}{\text{CEC at pH 7 or 8.2}} \times 100 \]

The pH used for cation exchange capacity (CEC) must be specified whenever the concept is to be used [13]. The base saturation philosophy is based on the principle that the maximum crop yields can be achieved by creating an ideal ratio of Ca, Mg, and K in the soil [14]. Figure 6 shows the relationship between the soil base saturation and the grain yield of common bean grown on an Oxisol of central Brazil. The maximum grain yield of this crop was achieved at 55% base saturation. Aluminum saturation is another index of soil acidity. The purpose of the aluminum saturation index is to provide a basis for lime recommendations aimed at reducing the toxic effects of Al as opposed to indices aimed at raising soil pH. The following equation illustrates the kinds of reactions that follow the addition of lime to an acid soil:

\[ 2\text{Al-x} + 3\text{CaCO}_3 + 6\text{H}_2\text{O} \rightleftharpoons 3\text{Ca-x} + 2\text{Al(OH)}_3 + 3\text{H}_2\text{O} + 3\text{CO}_2 \]

**Figure 6** Relationship between base saturation and grain yield of common bean grown on an Oxisol of central Brazil. (Adapted from Ref. 47.)
In this equation, -x denotes an exchange site on soil solids. The reaction detoxifies aluminum by binding it to hydroxyls, causing it to become insoluble in water. Although there are many compounds that can replace Al on the exchange sites, only those that also react with hydrogen make effective liming material.

Aluminum saturation can be calculated from the following formula:

$$\text{Al saturation} = \frac{\text{Al}}{\sum \text{Ca, Mg, K, Al}} \times 100$$

Values of Al saturation can be used as an index of the lime application rate that varies from soil to soil and among crop species as well as within cultivars of the same species. Figure 7 shows the relationship between Al saturation in a lowland acid soil of Brazil and the relative grain yield of common bean. With increasing Al saturation, there was a quadratic decrease in the grain yield. The critical Al saturation values for important field crops are listed in Table 2.

Soil pH is also used as an acidity index for determining the liming rate. The optimal soil pH is the minimum pH above which liming will not increase crop yield. This is normally called the “critical” pH [15]. Figure 8 shows the relationship between the pH and the dry matter yield of wheat (*Triticum aestivum* L.), corn, soybean, lowland rice, and common bean grown on an acid lowland Inceptisol soil of Brazil. The relative dry matter yield (DMY) of shoots of all the crops tested was significantly affected by soil pH. The optimal pH for the maximum DMY of wheat was 6.3, for soybean 5.6, corn 5.4, common bean 6, and for rice 4.9. This shows that crops responded differently to soil acidity. Among the crops tested, rice was the most tolerant and wheat was the most sensitive to soil acidity.

![Figure 7](image_url)
The quantity of lime added depends on the soil type, the quality of liming material, crop species, cultivars within species, and economic considerations. In Brazil, liming recommendations are based on soil exchangeable Al, Ca, and Mg. The lime requirement (LR) is calculated using the following formula:

\[
LR \text{ (metric tons ha}^{-1} \text{)} = \frac{\text{Al}^{3+} \times 2 + [2 - (\text{Ca}^{2+} + \text{Mg}^{2+})]}{2}
\]

The lime requirement computed from the Al, Ca, and Mg contents is based on the assumption that Al toxicity and Ca and Mg deficiencies are the most important growth-limiting factors in acid soils. In areas where lime is costly or dif-

<table>
<thead>
<tr>
<th>Crop</th>
<th>Type of soil</th>
<th>Critical Al saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cassava</td>
<td>Oxisol/Ultisol</td>
<td>80</td>
</tr>
<tr>
<td>Upland rice</td>
<td>Oxisol/Ultisol</td>
<td>70</td>
</tr>
<tr>
<td>Cowpea</td>
<td>Oxisol/Ultisol</td>
<td>55</td>
</tr>
<tr>
<td>Cowpea</td>
<td>Oxisol</td>
<td>42</td>
</tr>
<tr>
<td>Peanut</td>
<td>Oxisol/Ultisol</td>
<td>65</td>
</tr>
<tr>
<td>Peanut</td>
<td>Xanthic Halpludox</td>
<td>54</td>
</tr>
<tr>
<td>Soybean</td>
<td>Oxisol</td>
<td>19</td>
</tr>
<tr>
<td>Soybean</td>
<td>Xanthic Halpludox</td>
<td>27</td>
</tr>
<tr>
<td>Soybean</td>
<td>Oxisol/Ultisol</td>
<td>15</td>
</tr>
<tr>
<td>Soybean</td>
<td>Not given</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Soybean</td>
<td>Ultisol</td>
<td>20 to 25</td>
</tr>
<tr>
<td>Soybean</td>
<td>Histosol</td>
<td>10</td>
</tr>
<tr>
<td>Soybean</td>
<td>Ultisol</td>
<td>20</td>
</tr>
<tr>
<td>Corn</td>
<td>Oxisol</td>
<td>19</td>
</tr>
<tr>
<td>Corn</td>
<td>Xanthic</td>
<td>27</td>
</tr>
<tr>
<td>Corn</td>
<td>Oxisol/Ultisol</td>
<td>29</td>
</tr>
<tr>
<td>Corn</td>
<td>Oxisol/Ultisol</td>
<td>25</td>
</tr>
<tr>
<td>Corn</td>
<td>Oxisol</td>
<td>28</td>
</tr>
<tr>
<td>Mungbean</td>
<td>Oxisol/Ultisol</td>
<td>15</td>
</tr>
<tr>
<td>Mungbean</td>
<td>Oxisol/Ultisol</td>
<td>5</td>
</tr>
<tr>
<td>Coffee</td>
<td>Oxisol/Ultisol</td>
<td>60</td>
</tr>
<tr>
<td>Sorghum</td>
<td>Oxisol/Ultisol</td>
<td>20</td>
</tr>
<tr>
<td>Common bean</td>
<td>Oxisol/Ultisol</td>
<td>10</td>
</tr>
<tr>
<td>Common bean</td>
<td>Oxisol/Ultisol</td>
<td>8 to 10</td>
</tr>
<tr>
<td>Common bean</td>
<td>Oxisol/Ultisol</td>
<td>23</td>
</tr>
<tr>
<td>Cotton</td>
<td>Not given</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

*Source:* Adapted from Ref. 14.
CaCO₃ equivalent (t ha⁻¹) = 1.8 [Al − CAS(ECEC)/100]

where CAS is the critical aluminum saturation of the effective cation exchange capacity (ECEC). The ECEC is the sum of exchangeable Al, Ca, Mg, and K in cmolc kg⁻¹ of soil in the 1 M KCl extract at the original soil pH.

In some parts of Brazil, base saturation is being used as a parameter to calculate lime requirement using the following formula:

\[ LR \text{ (metric tons ha}^{-1} \text{)} = \frac{EC(B_2 - B_1)}{TRNP} \times df \]

where EC is the total exchangeable cations (Ca²⁺ + Mg²⁺ + K⁺ + H⁺ + Al³⁺) in cmolc kg⁻¹, \( B_2 \) is the optimal base saturation, \( B_1 \) is the existing soil base saturation, TRNP is the total relative neutralizing power of liming material, and df is the soil depth factor (1.0 for 20 cm, 1.5 for 30 cm depth). For Brazilian Oxisols, the optimal base saturation for most annual crops is considered to be in the range of 50 to 60% [16].

Figure 8 shows the relationship between soil pH and relative dry matter yield of five annual crops grown on an Inceptisol of Brazil. (Adapted from Ref. 81.)
2.2 Use of Gypsum

Gypsum (CaSO₄·2H₂O) has been used to alleviate both physical and chemical growth-limiting factors for roots [17]. Radcliffe et al. [18] reported that gypsum increased the subsoil root growth, which, in turn, improved water and nutrient uptake. In some cases, base cation leaching is desirable when the depth of rooting of Al-sensitive crops is limited by high Al saturation in the subsoil. Calcium accumulation in deeper layers can reduce the effects of subsoil acidity, thus allowing deeper crop root growth to tap into subsoil water during periods of surface soil moisture deficit [19]. The amount and the degree of cation leaching in soils of the humid tropics range widely, reflecting various factors that control leaching. For example, Ca movement is promoted by applying Ca in forms that include a mobile anion, such as CaSO₄·2H₂O (gypsum) or CaCl₂, rather than as CaCO₃ (lime).

In cerrado soils of Brazil, gypsum is recommended for annual crop production on the basis of clay content using the formula [20]:

\[
\text{Gypsum requirement (kg ha}^{-1}\text{)} = 50 \times \text{clay content (\%)}
\]

In addition to Ca, gypsum can supply S to growing plants and Ca can leach to subsoil horizons where native Ca levels may be too low to support root growth. The ionic strength of the soil solution is increased by gypsum, and the increased strength lowers the activity of Al³⁺. Furthermore, sulfate forms ion pairs with Al, such as AlSO₄⁺, which is nontoxic to plants [21].

2.3 Use of Optimal Rate of Essential Nutrients

Three main criteria can be used in defining an adequate rate of essential nutrients. The first criterion is the soil test calibration data relating nutrient concentration and crop response. This approach is applicable to immobile nutrients in the soil–plant system. In case of mobile nutrients such as N, the soil test calibration data have little use, and crop response curves relating the N rates and the yield should be more useful in making N fertilizer recommendations. Conducting soil and plant analysis is the other approach that can be used in determining optimal rates of essential nutrients in crop production and maintaining the sustainability of agricultural systems [22].

2.4 Nitrogen Deficiency

Nitrogen deficiency is a major limitation to plant growth on acid soils in both tropical and temperate regions. In tropical America, N deficiency is a major soil constraint over 93% of the region occupied by Oxisols and Ultisols [23]. The main reasons for widespread N deficiency in these and other similar regions in the tropics are (1) a lower rate of N application than the amount removed in harvested crops or lost by other processes and (2) the decreases in organic matter content
with successive cultivation. Table 3 shows the response of rice and common bean crops to fertilization on cerrado and varzea soils of Brazil. Similarly, Table 4 shows the response of flooded rice to N application on a varzea soil. The rice crop responded significantly up to 210 kg N ha\(^{-1}\); however, 90% of the maximum yield was obtained at about 100 kg N ha\(^{-1}\). Brazilian farmers use only an average of 60 kg N ha\(^{-1}\) for flooded rice.

### Table 3  Response to Fertilization of Rice and Common Bean Grown in Rotation in Cerrado and Varzea Acid Soils

<table>
<thead>
<tr>
<th>Fertility level</th>
<th>Rice grain yield (t ha(^{-1}))(^a)</th>
<th>Common bean grain yield (t ha(^{-1}))(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerrado soil(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>1.7b</td>
<td>1.2c</td>
</tr>
<tr>
<td>Medium</td>
<td>2.1a</td>
<td>1.8b</td>
</tr>
<tr>
<td>High</td>
<td>2.1a</td>
<td>2.2a</td>
</tr>
<tr>
<td>Medium + green manure</td>
<td>2.4a</td>
<td>1.5a</td>
</tr>
<tr>
<td>(F) test(^c)</td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>Varzea soil(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>4.3b</td>
<td>2.9b</td>
</tr>
<tr>
<td>Medium</td>
<td>5.5a</td>
<td>6.6a</td>
</tr>
<tr>
<td>High</td>
<td>5.5a</td>
<td>8.5a</td>
</tr>
<tr>
<td>Medium + green manure</td>
<td>6.3a</td>
<td>8.2a</td>
</tr>
<tr>
<td>(F) test(^c)</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

\(^a\) Values are averages of three crops grown in rice–bean rotation. *, **, Significant at the .05 and .01 probability levels, respectively. Within the same column, means followed by the same letter do not differ significantly at the .05 probability level by Tukey’s test.

\(^b\) Cerrado soil fertility levels for rice were low (without addition of fertilizers), medium (50 kg N ha\(^{-1}\), 26 kg P ha\(^{-1}\), 33 kg K ha\(^{-1}\), 30 kg ha\(^{-1}\) fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level). *Cajanus cajan* L. was used as a green manure at the rate of 25.6 t ha\(^{-1}\) green matter. For common bean, the fertility levels were low (without addition of fertilizers), medium (35 kg N ha\(^{-1}\), 44 kg P ha\(^{-1}\), 42 kg K ha\(^{-1}\), 30 kg ha\(^{-1}\) fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level).

\(^c\) Varzea soil fertility levels for rice were low (without addition of fertilizers), medium (100 kg N ha\(^{-1}\), 44 kg P ha\(^{-1}\), 50 kg K ha\(^{-1}\), 40 kg ha\(^{-1}\) fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level). *Cajanus cajan* L. was used as a green manure at the rate of 28 t ha\(^{-1}\) green matter. For common bean, the fertility levels were low (without addition of fertilizers), medium (35 kg N ha\(^{-1}\), 52 kg P ha\(^{-1}\), 50 kg K ha\(^{-1}\), 40 kg fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level).

Source: Adapted from Refs. 6 and 79.
Fractional application of N is an important management practice to improve N-use efficiency and improve crop yields. There was a significant difference in the grain yield when N was added in several applications during the lowland rice growth (Table 5). The addition of soluble salts of Ca, Mg, and K may also improve N fertilizer efficiency by reducing the soil solution pH. In a series of studies, Fenn et al. [24–26] found that adding soluble Ca salts to soils actually decreased NH$_3$ volatilization from surface urea applications and postulated that the added Ca$^{2+}$ would precipitate with carbonate formed during urea hydrolysis, removing Ca$^{2+}$ from the exchange complex.

Foliar application of urea has been demonstrated to be an effective method of nitrogen fertilization for cereals since the 1950s [27]. It has been suggested that there are several potential benefits of providing N to cereals via the foliage as urea solution. These include (1) reduced nitrogen losses through leaching, volatilization, and denitrification compared with N fertilizer applications to the soil; (2) the ability to provide N when root activity is impaired, e.g., in saline or dry conditions; and (3) uptake late in the season to increase grain nitrogen concentration [27].

<table>
<thead>
<tr>
<th>N rate (kg ha$^{-1}$)</th>
<th>1st crop</th>
<th>2nd crop</th>
<th>3rd crop</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.6</td>
<td>3.8</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>30</td>
<td>3.9</td>
<td>5.0</td>
<td>4</td>
<td>4.3</td>
</tr>
<tr>
<td>60</td>
<td>5.4</td>
<td>6.2</td>
<td>5.3</td>
<td>5.6</td>
</tr>
<tr>
<td>90</td>
<td>5.9</td>
<td>5.9</td>
<td>5.1</td>
<td>5.6</td>
</tr>
<tr>
<td>120</td>
<td>6.2</td>
<td>7.0</td>
<td>5.6</td>
<td>6.3</td>
</tr>
<tr>
<td>150</td>
<td>6.4</td>
<td>6.9</td>
<td>5.7</td>
<td>6.4</td>
</tr>
<tr>
<td>180</td>
<td>7.1</td>
<td>6.5</td>
<td>5.5</td>
<td>6.4</td>
</tr>
<tr>
<td>210</td>
<td>6.9</td>
<td>7.0</td>
<td>5.3</td>
<td>6.4</td>
</tr>
</tbody>
</table>

*F* test (N) ** ** ** **

*F* test (Crop) **

*F* test (N × Crop) *

CV (%) 8 10 12 10

Regression

<table>
<thead>
<tr>
<th></th>
<th>1st crop</th>
<th>2nd crop</th>
<th>3rd crop</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_0$</td>
<td>3.40</td>
<td>3.90</td>
<td>3.56</td>
<td>3.62</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>-0.00008</td>
<td>-0.0001</td>
<td>-0.00009</td>
<td>-0.00009</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.96**</td>
<td>0.91**</td>
<td>0.91**</td>
<td>0.96**</td>
</tr>
</tbody>
</table>

*, **: Significant at the .05 and .01 probability levels, respectively.

Source: Adapted from Ref. 47.
Cyanobacteria contribute to the N economy of flooded rice fields by reducing N\(_2\) to NH\(_3\). Several improved mutant N\(_2\)-fixing prokaryotes with the ability to excrete NH\(_3\) have been produced, including mutants of *Klebsiella pneumoniae* [28], *Nostoc muscorum* [29], *Spirillum lipoferum* [30], and *Azotobacter* species [31]. Spiller et al. [32] produced a nitrogenase-derepressed mutant strain of the cyanobacterium *Anabaena variabilis* (strain AS-1) that is capable of excreting NH\(_3\) produced by nitrogenase. Kamuru et al. [33] reported that the contribution of the mutant cyanobacterium to growth and yield of rice plants was equivalent to the application of 71 to 73 kg N ha\(^{-1}\) as (NH\(_4\))\(_2\)SO\(_4\). These authors also reported that the NH\(_3\)-excreting strain of *A. variabilis* shows potential for development for use as a biofertilizer in paddy rice production in areas where inorganic fertilizer N is unavailable or expensive and in rice production systems that aim to minimize environmental pollution from inorganic N fertilizers.

The nutrient budgets for sub-Saharan Africa show a net annual depletion of N, P, and K as a result of long-term cropping with little or no external nutrient input [34]. This depletion of soil nutrients is particularly high in the densely populated humid and subhumid highlands of East Africa [35,36]. Highlands (altitude

---

**TABLE 5** Lowland Rice Grain Yield Under Different Timing of N Application on an Acid Inceptisol of Central Brazil

<table>
<thead>
<tr>
<th>Nitrogen application timing(a)</th>
<th>Location 1 (t ha(^{-1}))</th>
<th>Location 2 (t ha(^{-1}))</th>
<th>Average (t ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T1</strong></td>
<td>7.1bc</td>
<td>7.2a</td>
<td>7.2ab</td>
</tr>
<tr>
<td><strong>T2</strong></td>
<td>7.8a</td>
<td>7.0ab</td>
<td>7.4a</td>
</tr>
<tr>
<td><strong>T3</strong></td>
<td>7.7a</td>
<td>6.9ab</td>
<td>7.3a</td>
</tr>
<tr>
<td><strong>T4</strong></td>
<td>7.3abc</td>
<td>6.8ab</td>
<td>7.1ab</td>
</tr>
<tr>
<td><strong>T5</strong></td>
<td>7.5ab</td>
<td>6.7ab</td>
<td>7.1ab</td>
</tr>
<tr>
<td><strong>T6</strong></td>
<td>7.3abc</td>
<td>7.0ab</td>
<td>7.2ab</td>
</tr>
<tr>
<td><strong>T7</strong></td>
<td>6.9c</td>
<td>6.7b</td>
<td>6.8b</td>
</tr>
</tbody>
</table>

\(F\) test (treatment): ** ** *, ** **

CV (%) 7 8 8

\(a\) The 90 kg N ha\(^{-1}\) application timing was (1) total at sowing (T\(_1\)); (2) one-third at sowing + one-third at active tillering + one-third at panicle initiation (T\(_2\)); (3) one-half at sowing + one-half at active tillering (T\(_3\)); (4) one-half at sowing + one-half at panicle initiation (T\(_4\)); (5) two-thirds at sowing + one-third at active tillering (T\(_5\)); (6) two-thirds at sowing + one-third at panicle initiation (T\(_6\)); and (7) one-third at sowing + two-thirds at the start of tillering (T\(_7\)).

*, **: Significant at the .05 and .01 probability levels, respectively. Means in the same column followed by the same letter are not significantly different at the .05 probability level by Tukey’s test. Values in the column for each location are averages of 2 years of field experimentation.

*Source*: Adapted from Ref. 78.
1200 to 3300 m) represent only about 20% of the total land area in East and Central Africa, but they contain about 60% of the population [37]. Although much of the highlands has a high potential for food production because of favorable seasonal precipitation, many of the soils are deficient in nutrients, particularly P [38,39]. In addition to the nutrient-depleting effects of long-term cropping, low native soil P and high fixation of P contribute to P deficiency in the highlands [40,41]. An essential ingredient for increasing crop yields in the highlands, therefore, is to increase the supply of plant-available P [39,42].

2.5 Phosphorus Deficiency

Phosphorus deficiency has generally been identified as one of the major limiting factors for crop production in highly weathered soils such as Oxisols and Ultisols in the tropics [23,43]. There is low natural P as well as low availability of P in these soils due to the reaction of soluble P with iron and aluminum oxides [11]. Phosphorus deficiency is one of the most yield-limiting factors for crop production on cerrado as well as varzea soils of Brazil [44,45]. The two main reasons for the occurrence of P deficiency in these acid soils are a low native soil P content and a high P fixation capacity. The P fixation capacity of an Oxisol from central Brazil was studied over a period of 80 days by Fageria and Barbosa Filho [46], who concluded that the amount of P fixed (i.e., not recovered by Mehlich-1 extracting solution) increased from 45 to 268 kg P ha\(^{-1}\) when the P application rate was increased from 50 to 400 kg P ha\(^{-1}\). This means these types of soils require large amounts of fertilizer P for optimal crop production.

When extractable soil P increased, grain yield of common bean grown on an Inceptisol of central Brazil increased significantly in a quadratic fashion (Fig. 9).

![Figure 9](image)

**Figure 9** Relative grain yield response of common bean to Mehlich-1 extractable soil P in an acid Inceptisol of central Brazil. (Adapted from Ref. 80.)
Similarly, Fageria et al. [45] reported a significant increase in grain yield of lowland rice with increasing P levels in these soils. Four categories were established for the P soil test: very low (VL), low (L), medium (M), and high (H) in relation to grain yield response zones (where VL/L = 0 to 70% relative grain yield, L/M = 70 to 95%, M/H = 95 to 100%, and H = 100%). The sufficiency P level is generally defined as 90 to 95% relative yield and coincides with the low limit of the medium or optimal range. This is the standard convention for soil test calibration research. The soil P test availability indices and P fertilizer recommendations for common bean are presented in Table 6. Fageria et al. [45] also presented soil P test availability indices and P fertilizer recommendations for lowland rice grown on a Brazilian Inceptisol.

### Table 6: Mehlich-1 Soil Test P Availability Indices and P Fertilizer Recommendations for Common Bean Grown on an Acid Inceptisol of Central Brazil

<table>
<thead>
<tr>
<th>Soil P test (mg kg⁻¹)</th>
<th>P test interpretation</th>
<th>Relative yield (%)</th>
<th>Broadcast P application (kg ha⁻¹)a</th>
<th>Band P application for maximum yield (kg ha⁻¹)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–5.3</td>
<td>Very low</td>
<td>0–70</td>
<td>153</td>
<td>66</td>
</tr>
<tr>
<td>5.3–7.1</td>
<td>Low</td>
<td>70–95</td>
<td>245</td>
<td>44</td>
</tr>
<tr>
<td>7.1–9.0</td>
<td>Medium</td>
<td>95–100</td>
<td>332</td>
<td>44</td>
</tr>
<tr>
<td>&gt;9.0</td>
<td>High</td>
<td>100</td>
<td>&gt;332</td>
<td>22</td>
</tr>
</tbody>
</table>

a Rate required to achieve the soil P test category shown, not the rate for maximum yield at the given soil test category.

b Additional banding P rate required for maximum yield following broadcast fertilization with P to reach the soil test P level.

Source: Adapted from Ref. 80.

Similarly, Fageria et al. [45] reported a significant increase in grain yield of lowland rice with increasing P levels in these soils. Four categories were established for the P soil test: very low (VL), low (L), medium (M), and high (H) in relation to grain yield response zones (where VL = 0 to 70% relative grain yield, L = 70 to 95%, M = 95 to 100%, and H = 100%). The sufficiency P level is generally defined as 90 to 95% relative yield and coincides with the low limit of the medium or optimal range. This is the standard convention for soil test calibration research. The soil P test availability indices and P fertilizer recommendations for common bean are presented in Table 6. Fageria et al. [45] also presented soil P test availability indices and P fertilizer recommendations for lowland rice grown on a Brazilian Inceptisol.

### 2.6 Potassium Deficiency

The responses of annual crops to K fertilization are not as widespread and not as significant as the responses to N and P fertilization in cerrado and varzea soils of Brazil. Potassium, however, is absorbed in large quantities by annual crops, especially by high-yielding cultivars. A single upland rice crop grown on an Oxisol of cerrado soil producing 4.8 t ha⁻¹ of grains in about 130 days took up 159 kg N ha⁻¹, 13 kg P ha⁻¹, and 189 kg K ha⁻¹ [47]. This means that in situations where intensive agriculture is practiced, failure to replace K that is removed in harvested crop can result in K deficiency becoming a limitation to further crop production. Large positive responses of upland and lowland rice to K fertilization in cerrado and varzea soils of Brazil have been reported by Fageria et al. [48,49]. Three management practices can be used to improve K fertilizer use efficiency by plants.
growing on acid soils. First, K fertilizers should be applied at an economically feasible rate, bearing in mind the need, in the long term, to replace K lost through crop removal and leaching. Second, the incorporation of crop residues in the soil after harvest enables a substantial amount of the plant K to be recycled. Approximately 85 to 92% of the total K content remains in the shoot of cereals such as rice and corn and 54 to 65% remains in the shoot of legumes such as common bean and soybean [50]. The third practice involves the use of K-efficient cultivars that have increased K uptake efficiency [11].

2.7 Calcium, Magnesium, and Sulfur Deficiency

Deficiencies of Ca and Mg are important limitations to plant growth in acid soils. Depending on the yield and the particular crop, about 26 to 53 kg Ca ha\(^{-1}\) and 12 to 26 kg Mg ha\(^{-1}\) can be removed from an Oxisol of central Brazil [47]. Crop requirements of Ca and Mg in deficient soils can be fulfilled with the application of dolomitic lime and gypsum. The lime rates applied on Brazilian acid soils can increase exchangeable Ca significantly (Table 7). When corn was grown on this soil, liming increased the grain yield significantly. At 8 t ha\(^{-1}\) lime rate, the grain yield was 31% higher compared with control treatment. Adequate Ca and Mg levels as well as Ca and Mg were also determined for upland rice, common bean, corn, and soybean grown in sequence on a Brazilian Oxisol (Table 8), showing a variation from crop species to species. Upland rice was most tolerant to soil acidity and soybean was most sensitive. In some Brazilian cerrado soils with sulfate-S below 10 mg kg\(^{-1}\), crop responses to applied S have been reported [51]. In these

<table>
<thead>
<tr>
<th>Lime rate (t ha(^{-1}))</th>
<th>Ca (mmol c dm(^{-3}))</th>
<th>Grain yield (t ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>23</td>
<td>7.7</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>8.5</td>
</tr>
<tr>
<td>12</td>
<td>31</td>
<td>7.9</td>
</tr>
<tr>
<td>16</td>
<td>33</td>
<td>7.7</td>
</tr>
<tr>
<td>20</td>
<td>38</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Regression

\[ \beta_0 = 18.74 \]
\[ \beta_1 = 0.47 \]
\[ \beta_2 = -0.008 \]
\[ R^2 = 0.52** \]
\[ 0.48** \]

** Significant at the .01 probability level.
cases, crops were likely to benefit from the addition of S-containing fertilizers at the rates of 20 kg S ha$^{-1}$.

### 2.8 Micronutrient Deficiency

Micronutrient deficiencies in field crops have increased markedly because of intensive cropping systems, loss of topsoil layers by erosion, losses through leaching, liming of acid soils, a decreasing proportion of farmyard manure compared with chemical fertilizers, the increasing purity of chemical fertilizers, and use of marginal lands for crop production. The deficiency problem is also exacerbated by the high demand of modern crop cultivars for micronutrients. Relatively little research under field conditions has been conducted on micronutrient nutrition of field crops as compared with macronutrients.

#### Table 8  Relationship Between Exchangeable Ca and Mg Parameters ($X$) and Grain Yield ($Y$) of Upland Rice, Common Bean, Corn, and Soybean Grown on an Oxisol of Central Brazil

<table>
<thead>
<tr>
<th>Ca and Mg parameters</th>
<th>Regression equation</th>
<th>$R^2$</th>
<th>Adequate level$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Upland rice</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = 4029 + 43.1X - 0.84X^2$</td>
<td>0.20NS</td>
<td>19</td>
</tr>
<tr>
<td>Mg (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -2800 + 12.5X - 0.52X^2$</td>
<td>0.81**</td>
<td>12</td>
</tr>
<tr>
<td>Ca saturation (%)</td>
<td>$Y = 4071 + 31.4X - 0.48X^2$</td>
<td>0.22NS</td>
<td>21</td>
</tr>
<tr>
<td>Mg saturation (%)</td>
<td>$Y = -595 + 696.3X - 23.3X^2$</td>
<td>0.70**</td>
<td>15</td>
</tr>
<tr>
<td><strong>Common bean</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -1648 + 237.4X - 4.13X^2$</td>
<td>0.80**</td>
<td>29</td>
</tr>
<tr>
<td>Mg (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -16209 + 2844X + 113X^2$</td>
<td>0.43*</td>
<td>13</td>
</tr>
<tr>
<td>Ca saturation (%)</td>
<td>$Y = -1266 + 165X - 2.2X^2$</td>
<td>0.62**</td>
<td>37</td>
</tr>
<tr>
<td>Mg saturation (%)</td>
<td>$Y = -978 + 1429X - 44.4X^2$</td>
<td>0.40*</td>
<td>16</td>
</tr>
<tr>
<td><strong>Corn</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -139 + 497X - 7.5X^2$</td>
<td>0.73**</td>
<td>33</td>
</tr>
<tr>
<td>Mg (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -30640 + 5708X - 209X^2$</td>
<td>0.81**</td>
<td>14</td>
</tr>
<tr>
<td>Ca saturation (%)</td>
<td>$Y = 761 + 343X - 4.0X^2$</td>
<td>0.72**</td>
<td>43</td>
</tr>
<tr>
<td>Mg saturation (%)</td>
<td>$Y = -17743 + 2930X - 82.5X^2$</td>
<td>0.81**</td>
<td>18</td>
</tr>
<tr>
<td><strong>Soybean</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -131 + 81.7X - 1.03X^2$</td>
<td>0.96**</td>
<td>40</td>
</tr>
<tr>
<td>Mg (mmol$_c$ dm$^{-3}$)</td>
<td>$Y = -7735 + 1297X - 46.6X^2$</td>
<td>0.99**</td>
<td>14</td>
</tr>
<tr>
<td>Ca saturation (%)</td>
<td>$Y = -1.20 + 57.9X - 0.56X^2$</td>
<td>0.96**</td>
<td>52</td>
</tr>
<tr>
<td>Mg saturation (%)</td>
<td>$Y = -4782 + 693X - 19.2X^2$</td>
<td>0.99**</td>
<td>18</td>
</tr>
</tbody>
</table>

$^a$ Adequate level was calculated by regression equation where $R^2$ was significant. When $R^2$ was nonsignificant, original soil value was considered adequate.

*, ** Significant at the .05 and .01 probability levels, respectively.
Brazilian Oxisols and Ultisols are generally low in available Zn and B, and deficiency of these nutrients has been reported in upland and lowland rice, common bean, soybean, corn, and wheat [14,52]. This deficiency is due to low natural levels of Zn and B in these soils as well as worsening of the deficiency by liming. With increasing pH due to liming, the ionic forms of the micronutrient cations are converted to insoluble hydroxide or oxide compounds. In such a case, deficiency of micronutrients is expected. One typical example of this type is iron deficiency in Brazilian Oxisols in upland rice when soil pH is raised to around 6 [47]. The best management strategies are to avoid overliming these soils, maintaining the pH in the range 5.5 to 5.8. An application of about 2 to 5 kg Zn ha$^{-1}$ as Zn sulfate can correct Zn deficiency in most annual crops. Foliar spray of micronutrients is also an important strategy to correct micronutrient deficiency in annual crops [27,53].

2.9 Use of Farmyard Manures

Farmyard manure may be a complementary source of N, P, and K when applied at rates based on the composition of the manure and the nutrient-supplying potential of the soil [54,55] for crops grown on tropical soils for sustainable crop production. Opportunities for resource-poor farmers in the tropical regions to increase the application of high-quality manure may be limited, particularly in the absence of large numbers of improved breeds of livestock. However, a study conducted by Jama et al. [39] suggested that limited supplies of manure could be effectively integrated with commercial fertilizers, such as triple superphosphate and urea. Net benefits for integrated use of manure with triple superphosphate and urea remained positive and comparable to those for application of all the P and N as triple superphosphate and urea. Integration of manure with inorganic fertilizers may result in the benefits of greater residual effects of organic than inorganic sources and other advantages of manure in addition to a supply of P and N (e.g., improved soil physical properties and supply of basic cations) [56].

Crop nutrient imbalance and soil and water pollution can occur when the manure application rates are greater than the crop demand [57]. Manure application may also affect weed population dynamics. Pleasant and Schlater [58] reported that 1 kg of cow manure can contain up to 42 apparently viable seeds of lambsquarters (*Chenopodium album* L). After reviewing the relevant literature, Zimdahl [59] concluded that about 20% of the seeds of certain weed species are still viable after passage through cattle (*Bos* sp.), manure storage, and application.

2.10 Maintenance of Soil Organic Matter

Soil organic matter is not just the reservoir of nutrients and water but also improves soil structure, enhances activities of beneficial microorganisms, reduces elemental toxicity, and makes soil less susceptible to erosion. Therefore, improving and/or maintaining soil organic matter is one of the most important management
practices for maintaining fertility of tropical soils for sustainable crop production. Normally, the soil organic matter content of tropical soils decreases with cultivation. This decrease can be attributed to tillage and related soil erosion and oxidation [11]. Such a decline has emphasized the need for development of cropping systems and cultural practices that reduce soil erosion and increase soil organic matter. In humid regions where plant available water is sufficient for annual crop production, forage legumes are often used in the rotation to improve soil productivity through increased organic matter production and N₂ fixation. The practice of growing plants (such as legumes) to enhance soil productivity during the fallow period is called green fallow [60]. The benefit of legumes is attributed predominantly to increased N supply and enhanced soil quality [61].

Increased inputs of plant residues may improve the organic matter content of the soil, thus enhancing N conservation and improving soil structure. In addition, through incorporation of large amounts of organic C into soil, microorganisms may minimize residual NO₃⁻-N leaching from fertilizer application through immobilization of inorganic soil N [62]. The residue of high-yielding corn may account for as much as 5 to 10 t of dry matter ha⁻¹, with a C/N ratio of 40:1 to 60:1 [62]. This high C/N ratio provides a favorable condition for immobilization of N by microorganisms. The presence of ample C substrate can also cause rapid O₂ consumption, indirectly enhancing the potential for denitrification [63].

The major agent in organic matter destruction by crop production is tillage. Extensive soil tillage, which inverts or mixes the soil, introduces large amounts of oxygen into the soil and stimulates aerobic microorganisms to consume the organic matter as a food source. Use of no-till systems can reduce the rate of organic matter loss but cannot stop it completely. Crop rotations that involve long periods of sod, pasture, or hay crops usually increase soil organic matter content during these periods and thus influence subsequent crops beneficially and probably contribute to the positive rotation effect [64].

2.11 Improving Association with Mycorrhizal Fungi

The mycorrhizal relationship is thought to be important in nutrient and water uptake by plants. In tropical acid soils, a low level of P is a significant factor limiting plant growth. Just as bacteria are important for providing N to legumes through N₂ fixation, the proper selection of plants to maximize biological associations with beneficial arbuscular mycorrhizal fungi may be important for maintaining plant productivity in soils with low available P [65]. Mycorrhizal dependence [calculated as (the shoot dry weight of nonmycorrhizal / shoot dry weight of mycorrhizal plants) × 100%] quantifies the responsiveness to arbuscular mycorrhizal fungi [66]. Plant species as well as cultivars within species differ in their mycorrhizal dependence [67–70]. For example, soybean was more responsive to mycorrhiza than corn, but considerable variation occurred among soybean cultivars [69].
2.12 Exploring Plant Genetic Variability

Search for, and exploitation of, crops that are able to utilize poorly available nutrients is one strategy to improve sustainability of agriculture on marginal lands [71]. Use of nutrient-efficient or tolerant crop species and/or cultivars can be a complementary solution for crop production on low-fertility or acidic soils. Differences among crop cultivars in the efficiency of use of N, P, and K have been reported [14,50,72,73] under Brazilian conditions. Similarly, Table 2 shows differences in Al tolerance of different crop species expressed on the basis of Al saturation, with cassava, upland rice, cowpea, and peanut being most tolerant to Al toxicity and cotton, common bean, soybean, and mungbean being most sensitive.

Morphological characters such as root length, surface area, fineness (radius), and frequency of root hairs are considered to influence strongly P uptake [74]. Breeding programs aimed at developing genotypes with improved root morphology and increased contact area of root surface with soil are, therefore, considered vital in screening for P-efficient plants [75].

2.13 Other Cultural Practices

In addition to practices already discussed, nutrient uptake efficiencies of crops in tropical soils can be improved by adopting appropriate crop rotation, controlling soil erosion, using grass–legume bicultures, and controlling diseases, insects, weeds, and allelopathy. Detailed discussion of these practices under tropical conditions is given by Fageria and Gheyi [11], Fageria and Baligar [76], Fageria and Santana [77], and Fageria and Prabhu [78].

3 FAVORABLE SOCIOECONOMIC FACTORS FOR FARMERS

Favorable socioeconomic conditions (such as availability of agricultural credit at lower interest rates, reasonable price of agricultural produce, availability of fertilizers and other agricultural inputs in time, adequate transport and storage facilities, and availability of effective extension services) are some of the important factors that may govern the use of appropriate crop production technologies. If these factors are favorable, farmers are likely to use adequate production practice, which may result in a higher crop yield and a higher use of nutrients. These factors have a significant impact in adoption of appropriate technologies by farmers, particularly in developing countries [76].

4 CONCLUSIONS

The world population is expected to be about 8.5 billion in the year 2025 and more than 10 billion by the year 2050 [11]. Most of this population increase will be in the developing tropical regions. Food production in these areas needs to be in-
FIGURE 10  Integrated plant nutrient management system for sustainable crop production. (Adapted from Ref. 76.)
creased significantly to avoid hunger and malnutrition and social disorder. Therefore, the production per unit area needs to increase, and new areas have to be brought under cultivation. Because of a relatively low yield and a sufficient land area available in the tropics, there is a large potential to increase world food production. Tropical soils represent one of the largest reserves of the agricultural lands of the world that can be brought under agricultural production. These lands are an important natural resource in the biosphere, but they need to be managed with great care.

Acid, low-fertility soils in tropics (mainly classified as Oxisols and Utisols) cover 43% of the area. Improving the fertility of these soils is the first prerequisite to bringing them under cultivation for sustainable crop production. Important strategies are liming; use of adequate fertilizer rates at appropriate times during crop growth; maintenance of adequate soil moisture; conservation tillage; maintenance of soil organic matter content; reducing infestation of insects, diseases, and weeds; crop rotation; and planting nutrient-efficient and acidity-tolerant crop species and cultivars within species. Control of allelopathy and favorable socioeconomic factors for farmers are important management strategies for improving the fertility of these soils. An integrated nutrient management system should be adopted in improving the nutrient use efficiency of annual crops (Figure 10).

To put these management strategies into practice, it is necessary to use research data to provide technological packages to the farmers that may vary according to different agroecological regions as well as social and economic conditions of the farmers. Therefore, to achieve meaningful results, there is a need for synergy between research and extension, with financial support from the government as well as private agribusiness.

REFERENCES

5. RJ Buresh, PA Sanchez, FG Calhoun. Replenishing Soil Fertility in Africa. Soil Sci-


47. NK Fageria. Annual report of the project: the study of liming and fertilization for rice and common bean in cerrado region. National Rice and Bean Research Center, Santo Antonio de Goias, Brazil, 1998.


Role of the Genotype in Tolerance to Acidity and Aluminum Toxicity

David F. Garvin
Plant Science Research Unit, USDA-ARS, St. Paul, Minnesota, U.S.A.

Brett F. Carver
Oklahoma State University, Stillwater, Oklahoma, U.S.A.

1 INTRODUCTION

The agronomic challenges associated with acid soils have brought plant breeders into a research arena often considered a principal concern of soil fertility and plant nutrition specialists. Their approaches, while quite different, have the same intent: to bring actual crop yields closer to potential yields by modifying the plant genotype or the soil environment. Soil acidification places productivity of currently cultivated lands at risk. As cultivation continues, the likelihood increases that nutrient toxicities and deficiencies associated with low pH will erode yield potential.

Nowhere is this more apparent than in the surface-acidified areas of the U.S. southern Great Plains, site of some of the world’s most intensive wheat (*Triticum aestivum* L.) production. As in other wheat-growing areas, such as Australia and South Africa, natural soil acidification is accelerated by removal of basic cations through the harvesting of vegetation and grain. Even during a period of the most intensive liming application in the U.S. Great Plains, the proportion of wheat fields with strongly acidic pH has actually increased, while those with neutral or...
alkaline pH has decreased [1]. Apparently, continuous wheat production has increased soil acidification faster than the addition of lime has diminished it.

In this chapter, we intend to showcase one of nature’s gifts—genetic variability—as one of the many resources available for reducing crop losses with soil acidity. We present our case not to argue genetic modification as an alternative to lime application or other soil-ameliorative approaches but as a necessary partner to them. Our discussion will center on aluminum (Al) tolerance as the central component of acid soil tolerance, not to exclude other legitimate trait systems that might be targeted in plant breeding programs, such as P utilization efficiency and Mn tolerance. Plant breeders have traditionally emphasized Al tolerance because it often evolves in plant materials common to acid soil environments.

2 SOIL ACIDITY AND GENETIC REMEDY

Two genetic forces generally provide the foundation for most crop improvement programs: extension of yield potential (assuming yield is the economic target) and reduction of susceptibility to biotic and abiotic stresses. Keeping these forces in balance is critical. Let one outweigh the other, and progress will suffer, if not cease. Improving yield via plant breeding can be compared with lifting a heavy paper sack full of groceries. The groceries inside the sack may symbolize the total yield variability or distribution from which the breeder selects. At the top of the sack is potential yield, or that which is expressed in the absence of stress, and at the bottom is yield resulting from tolerance to stress. Breeders can, and certainly do, improve yield by lifting the sack from the top—the more tempting approach and perhaps most convenient—or they may improve yield by lifting from the bottom, which tediously requires both hands but provides more stable support. One can only go so far before the sack tears if it is lifted solely from the top, i.e., if genetic progress depends solely on selection for yield potential. This analogy is especially fitting for breeding programs that target production zones limited by soil acidity. Yield potential means nothing when the plant is not properly equipped with a genetic mechanism that confers tolerance to critically acid soils.

Wheat cultivars currently grown throughout the Great Plains often yield in excess of 5 to 7 t ha\(^{-1}\) under optimal pH, but the same cultivars may yield nothing on acid soils in neighboring fields with critical soil acidity. As an example, we show in Table 1 the grain yield of the most popular bread wheat cultivars grown in the southern Great Plains today when measured under irrigation in the western High Plains area (near Guymon, Oklahoma, pH 7.1, minimal abiotic stress) versus under dryland conditions near Enid, Oklahoma, where low soil pH (pH 4.1, Al saturation >30%) is the predominant yield-suppressing factor. Yield potential, as approximated at Guymon, is independent of yield performance under soil acidity. Custer, the second leading cultivar currently planted in Oklahoma, has extremely high yield potential but lacks the required tolerance to low pH to be planted in all-
most 20% of Oklahoma’s wheat acreage. Tolerant and sensitive cultivars may differ by as much as 3 t ha\(^{-1}\) under the acidic conditions described here, yet, as this chapter will show, their genotypic differences may be limited to a few loci relative to Al tolerance. Rarely do breeders have the capacity to manipulate a small number of genes with such enormous impact on traits of economic importance.

Genetic improvement of tolerance to soil acidity has taken on high priority in breeding programs for several major field crops grown in the United States, including alfalfa, *Medicago sativa* L. (Bouton et al., http://genes.alfalfa.ksu.edu/TAG/TAGpapers/Bouton/BoutonAlPaper.htm, March 29, 2000); soybean, *Glycine max* (L.) Merr. [2]; and winter wheat, *Triticum aestivum* L. [3]. Breeding programs have long been established in other countries for improving acid soil tolerance of maize [4] and spring wheat [5]. We searched the Current Research Information System (CRIS) to locate other USDA-CSREES and USDA-ARS–supported research programs that specifically identify acid soil tolerance as a breeding objective. Those identified include the hard winter wheat breeding program at Kansas State University (directed by A. Fritz); the cereal breeding program at University of Georgia, Griffin (directed by J.W. Johnson); and the winter wheat and ryegrass breeding programs at Texas A&M University, Overton (formerly directed by L.R. Nelson).

Genetic remediation offers several benefits complementary to, or independent of, soil amelioration. Genetic tolerance may be the most practical and economic approach in cases where tenants with short-term leases do not wish to com-

<table>
<thead>
<tr>
<th>Cultivar</th>
<th>Nonacidic (kg ha(^{-1}))</th>
<th>Acidic (kg ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Custer</td>
<td>5920</td>
<td>1550</td>
</tr>
<tr>
<td>Chisholm</td>
<td>5240</td>
<td>2050</td>
</tr>
<tr>
<td>2174</td>
<td>4850</td>
<td>2400</td>
</tr>
<tr>
<td>Tomahawk</td>
<td>4740</td>
<td>890</td>
</tr>
<tr>
<td>Oro Blanco</td>
<td>4680</td>
<td>2320</td>
</tr>
<tr>
<td>Jagger</td>
<td>4620</td>
<td>3100</td>
</tr>
<tr>
<td>2137</td>
<td>4620</td>
<td>2790</td>
</tr>
<tr>
<td>LSD (0.05)</td>
<td>810</td>
<td>400</td>
</tr>
</tbody>
</table>

* Expected yield in the absence of acid soil stress at Enid would be approximately 3300 kg ha\(^{-1}\).
mit to long-term investment of one or more liming applications. Tolerance may also provide immediate results in crop performance that may not be realized immediately following lime application, depending on the degree of its incorporation, activation, and movement to subsurface regions. Genetic tolerance provides protection throughout the acidified zone, not only the zone of amelioration. Thus, an effective strategy might be to use acid soil–tolerant cultivars with surface lime application [6,7]. Excessive liming, or restoration of soil pH beyond the recommended level, may cause undesirable shifts in soil pathogen populations, thereby causing higher disease pressure. This yield reversal has been observed in wheat in association with take-all disease, caused by *Gaeumannomyces graminis* var. *tritici* Walker, and possibly in combination with other soilborne pathogens [8,9]. For this reason, the true response to liming has often been difficult to quantify for wheat grain yield in the southern Great Plains. Krenzer and Westerman [10] first reported only a slight increase in grain yield between nonlimed plots (pH 4.6) and plots that received 25% of the soil buffer index recommendation value. Plots receiving twice the rate actually declined in grain yield compared with the nonlimed plots. After their results were reported, infection by *Rhizoctonia cerealis*, the causal organism for sharp eye-spot disease, was found to be more severe in the limed plot areas (E.G. Krenzer, personal communication, 2000). Soil pH is not believed to have a direct effect on the root rot pathogen but may alter the soil microflora to allow the pathogen to flourish (L.R. Singleton and R.M. Hunger, personal communication, 2000). Because no effective level of resistance has yet been found in winter wheat for take-all and other root rot diseases, the adoption of acid soil–tolerant genotypes becomes even more important in managing acid soils that may harbor root rot pathogens. Finally, although any soil amendment may be effective in mitigating the effect of low pH, its coverage may not be spatially uniform across the area of production.

These scenarios point to varietal selection as a management tool, or a form of “insurance,” for managing acid soils. Survey data for cultivars under cultivation in the southern Great Plains bear witness to the importance of acid soil tolerance in varietal choices made by farmers. Since 1994, the leading wheat cultivars based on acreage seeded in Oklahoma have consistently and noncoincidentally featured a high degree of Al tolerance [1].

Genetic variation for tolerance to acid soils and its chemical components have been demonstrated in a plethora of cultivated and pasture crops, thanks largely to the work of USDA-ARS scientists Dr. Charles Foy and Dr. V.C. Baligar. Foy [11] cited and summarized the research on genotypic ranges of tolerance in several plant species. Davidson [12] also summarized differences in Al and Mn toxicity tolerance for several crop and pasture species. One must interpret interspecific comparisons with caution, however, because they can be greatly skewed by wide intraspecific variability and limited intraspecific sampling of genotypes used in the bioassay. For the same reason, phytotoxicity for a range of soils is not
well predicted by the genotype(s) of a species sampled to make the prediction [13]. One message is clear from the extensive database created on genetic divergence for acid soil tolerance: the levels of genetic diversity are conducive to crop improvement via traditional hybridization and phenotypic selection of unique gene combinations. Recent advances in molecular genetics will make manipulation of the plant genotype an even more effective approach to alleviating soil acidity.

3 VARIABILITY FOR ALUMINUM TOLERANCE AND ITS GENETIC BASIS: THE CASE OF WHEAT

Genetic variation allows different plant species, and different cultivars of the same species, to exhibit differing abilities to grow in acid soils. The discovery of genetic variation for Al tolerance in wheat dates back nearly 100 years, when it had a prominent role in the earliest breeding efforts in Brazil and was instrumental to the expansion of wheat production in that country. A historical view of these breeding efforts, found in publications by Da Silva [14] and Beckmann [15], is briefly summarized here because of their relevance to later discussions of the genetics of Al tolerance in this crop.

In the early 1900s, wheat breeding efforts were initiated in areas of southern Brazil that suffered from severe soil acidity and Al toxicity. Significant variation among different wheat cultivars for a trait referred to as “crestamento,” which roughly translates in English to “partially burned,” was well known. At that time, the basis for crestamento was not known, although we now know it is a symptom elicited by toxic levels of Al in the soil. These effects were so great in some of these areas that selection against wheat cultivars sensitive to Al was generally 100%, with the plants dying before yielding any grain. However, a range of tolerance to crestamento in wheat was reported to exist among the cultivars that were being evaluated at the time.

Because of the strong association between tolerance to crestamento and superior performance, Al tolerance was, by default, probably the earliest trait selected for by the southern Brazilian wheat breeding programs, dating as far back as the early 1920s. One particular cultivar, Polyssu (named after the person who had identified the cultivar in a wheat field in 1914), exhibited exceptional resistance to crestamento compared with other cultivars and was used in many early crosses to other wheat cultivars. In particular, Polyssu was crossed to a series of desirable lines from earlier breeding work, referred to collectively as “Alfredo Chaves” (AC) lines. The AC lines were named after the experiment station at which they were developed and presumably also possessed superior Al tolerance to be so productive on these soils. These Polyssu × AC crosses proved to be extremely important for Brazilian wheat production; most of the important Brazilian wheat cultivars arising over the next several decades (e.g., Frontana, Colonias,
Frontiera, Rio Negro, Maringa, Toropi, BH1146) could trace their parentage back to these crosses [16]. This shared lineage among historically important Brazilian cultivars reflects a uniquely high level of Al tolerance found in Polyssu or the AC lines. The importance of the Polyssu × AC crosses is not restricted to Brazilian agriculture. Indeed, as wheat-breeding efforts on acid soils expanded globally, Brazilian wheats derived from these crosses became a cornerstone source for genes that confer Al tolerance. Thus, the production of wheat on acid soils around the world has benefited greatly from the early discoveries and research of Brazilian wheat breeders.

As Al tolerance became more recognized as a trait of importance to wheat breeding in many regions of the world, efforts were made to explore existing variation for this trait. In particular, there was a flurry of research on this topic in the 1960s and 1970s, and interest persists to this day, as future agricultural expansion is likely to be on acidic soils because of their worldwide prevalence [17]. A general outcome of all of these studies is that Al tolerance variation, when measured as a metric character such as root growth, plant weight, or yield, cannot be defined on the basis of discrete genotypic classes but rather appears to be continuous [3,18–20]. Some authors have identified generic classes of Al tolerance, such as tolerant, intermediate, or sensitive, or with more classes [16,21–25], but these are classifications of convenience and have been based on ranges of values rather than clear discontinuities or thresholds that differentiate between the classes. One of the widely used bioassays for Al tolerance in cereals, the hematoxylin root staining assay, encourages discrete classification with its visual scale of assessment. Although it serves to predict gross differences in Al tolerance, the correlation of staining score with metric classifications that directly estimate Al tolerance is far from perfect [26], particularly when Al tolerance is measured under field conditions [27].

A number of interesting findings have emerged from studies of Al tolerance variation in wheat. For instance, several studies have revealed that variation for Al tolerance among wheat cultivars is correlated with their origin [19,28,29]. Cultivars from Brazil appear to be nearly uniformly Al tolerant and to possess the greatest degree of Al tolerance, and southeastern U.S. cultivars have also exhibited significant Al tolerance. Low levels of Al tolerance have been found in cultivars developed in the western United States and the Great Plains, although the trend in the Great Plains has recently reversed with more conscious selection for acid soil tolerance. Thus, historically, a ubiquitous feature of wheat improvement efforts on acidic soils appears to have been an unconscious selection for Al tolerance, with the degree of selection reflective of the severity of the Al toxicity in the region. In contrast, in the absence of Al toxicity, selection during wheat breeding has been based on other traits whose relative impact on phenotypic variation for performance may have been reduced in acid soils due to the large effect imposed by Al toxicity. Because Al tolerance is presumed to have a neutral effect in the absence of Al toxicity (see later), there is no reason for Al tolerance to persist in new germ
plasm developed from Al-tolerant cultivars on noncritically acid soils, unless by
chance or due to linkage to other desirable traits.

Another fact emerging from studies of Al tolerance variation in wheat is that
Al tolerance is not an inherent characteristic of wheat but rather represents a de-
rived state. This can be inferred from the simple observation that wheat as a rule
is not particularly Al tolerant and that Al tolerance is more the exception than the
rule. Further, studies of wild wheat [19,30] and durum (T. turgidum L. durum)
wheat [31] have been unsuccessful in finding levels of Al tolerance approaching
those found in bread wheat. Taken together, these observations suggest that hy-
bridization events that occurred between the diploid progenitors of wheat were not
between Al-tolerant landraces and that the rather restricted occurrence of extreme
Al tolerance that exists in wheat today is due to mutations that accrued after the
hexaploid genome of wheat was assembled through interspecific hybridization.
Perhaps Al tolerance existed in the early hexaploid wheats but was selected
against in early neutral-pH wheat production environments because of the
metabolic cost of the trait. However, our current understanding of the physiology
of Al tolerance in wheat indicates that the only definitive mechanism of Al toler-
ance in wheat is the exudation of malate from the terminal few millimeters of the
root apex, specifically in response to Al exposure [32], suggesting that Al toler-
ance is remarkably conservative relative to metabolic cost. Thus, the Al tolerance
trait is unlikely to have a deleterious cost to crop performance in neutral soils that
would render it subject to negative selection. This hypothesis is supported by re-
sults of field studies that do not show any trend toward poor performance of Al-
tolerant cultivars in the absence of Al toxicity [27,33].

To date, the various wild and domesticated species of wheat have been the
focus of more Al tolerance genetic studies than any other species. The ability to
trace the ancestry of the more extreme levels of Al tolerance in many Brazilian
wheat cultivars and cultivars from other areas back to Polyssu and/or Alfredo
Chaves, coupled with the apparent ease with which the trait can be completely
transferred through phenotypic selection, implies that extreme levels of Al toler-
ance may be under simple genetic control. Although some studies do support that
prediction, we still lack a clear and comprehensive picture of Al tolerance genet-
ics in wheat, even after decades of research into the topic. In part this can be at-
tributed to the fact that over the years, genetic studies have varied widely in choice
of genotype(s), although the tolerant standards for comparison often include At-
las 66 or BH1146. Further, these studies rely upon a diverse array of screening me-
dia and methods and Al levels with which to assess genotypes [3]. Thus, it is dif-
cult to assemble the results into a cohesive picture of Al tolerance. Regardless of
this obstacle, certain results do provide a foundation on which to begin to describe
the genetic basis for Al tolerance in wheat.

Perhaps the earliest attempts to describe Al tolerance inheritance in wheat
were conducted by Iwar Beckmann, one of the scientists behind the development
of the early Al-tolerant Brazilian cultivars. He observed that F2 populations derived from Al-tolerant versus Al-sensitive cultivars segregated 3:1 for tolerance as expected for a single dominant character, although he noted that there were many plants scored as “doubtful” as well [15]. Since then, many other studies have confirmed that, unlike tolerance to other soil-associated abiotic stresses such as salt toxicity, single major genes that confer a high degree of Al tolerance do exist in wheat.

The first inheritance study of Al tolerance in wheat to be formally reported in the literature was by Kerridge and Kronstad [34]. In an experiment elegant in its simplicity, they crossed the Al-tolerant wheat cultivar Druchamp and the Al-sensitive cultivar Brevor and analyzed the F2 population from this cross for root growth in hydroponic conditions in the presence or absence of Al. In its absence, the F2 population exhibited a rather narrow and continuous distribution for root growth with the mean approximately intermediate between the two parents. However, when a second set of F2 plants was grown in the presence of Al in the solution, a distinct bimodal distribution emerged, with approximately one fourth of the plants now exhibiting extremely limited root growth and being separated from the remaining three fourths of the plants by a clear discontinuity in the distribution curve. This characteristic 3:1 ratio of Al-tolerant versus Al-sensitive plants strongly supported the hypothesis that Al tolerance differences in the F2 were due to segregation for a single dominant gene. Later studies using hydroponic culture root measurements or other methods of assessing Al tolerance such as hematoxylin staining or acid soil growth bioassays have also confirmed the presence of major Al tolerance genes in populations segregating for Al tolerance [24,35–38]. Although these studies have generally used different tolerant and sensitive cultivars, in some instances the inheritance of the same cultivar has been examined by different groups in crosses with different Al-sensitive lines, and results have been consistent. For instance, different studies with the highly Al-tolerant cultivar BH1146 have suggested that its tolerance, or a large part of it, derives from a single major locus [24,36].

Whereas many studies have reported that Al tolerance follows a simple inheritance pattern, other studies have shown Al tolerance to represent the expression of two genes. The cultivar Atlas 66, an Al-tolerant cultivar developed in North Carolina and released in the 1940s, has more than once been suggested to possess more than one Al tolerance gene. This is based upon a 15:1 segregation for Al tolerance versus Al sensitivity in F2 populations from crosses between Atlas 66 and Al-sensitive wheat lines [36,37,39], although single-gene segregation was also observed depending on the sensitive parent used. This suggests that two dominant genes are present in Atlas 66 that can each confer Al tolerance. The fact that Al tolerance was conferred whether one or both genes were present in plants of the F2 population suggests that these genes do not act in a completely additive fashion. An examination of the pedigree of Atlas 66 indicates that the highly Al-
tolerant cultivar Frondoso was the likely donor of Al tolerance to Atlas 66. Frondoso traces its pedigree back to the Polyssu × AC crosses from early in the 20th century, which suggests that the Al tolerance of Atlas 66 also derives from these old Brazilian cultivars. Other studies have also reported digenic segregation in a population derived from an Al-tolerant versus Al-sensitive cross but with gene interactions [35]. Furthermore, the presence of more than one gene in a given Al-tolerant cultivar can be inferred from studies in which backcross introgression of Al tolerance from an Al-tolerant cultivar to an Al-sensitive cultivar has resulted in incomplete transfer of the trait [40,41].

Although these studies have provided insights into the genetics of Al tolerance, they simultaneously expose a paradox that has long faced scientists seeking to understand the genetics of Al tolerance—namely that Al tolerance is commonly inherited in a simple fashion in designed crosses; yet, as noted earlier, when Al tolerance is evaluated in a range of germ plasms, a broad and continuous distribution from highly tolerant to highly sensitive genotypes is observed, indicative of a complex multigene system with varying effects on Al tolerance. Thus, it is difficult to reconcile such findings with a generic genetic model in which one or a few loci control Al tolerance in wheat. To this day, this paradox represents a major unanswered question in Al tolerance genetics.

To examine further the issue of gene diversity for Al tolerance, it should first be recognized that the genetic basis of Al tolerance determined from an Al-tolerant × Al-sensitive cross can provide only limited insight into this issue, primarily because inferences are restricted to the cross in question. Instead, explorations of Al tolerance gene diversity can be adequately addressed only by genetic studies that either directly determine on a case-by-case basis whether Al tolerance between two Al-tolerant cultivars is due to the action of the same or a different locus or by statistical methods associated with quantitative genetics. In some instances, this has helped further our understanding of the genetic basis of Al tolerance, whereas in other instances it has revealed contradictory information.

Some efforts have been made to determine whether different Al-tolerant cultivars possess the same or different genes for Al tolerance. The ability to trace the pedigree of most highly Al-tolerant cultivars back to either Polyssu or one of the AC lines developed in Brazil, coupled with the ease with which this trait has been introgressed into other germ plasm, implies that highly Al-tolerant lines are likely to share a gene or a few genes for Al tolerance. By crossing these different Al-tolerant genotypes and examining derivative segregating populations for individuals that exhibit greater Al sensitivity than either parent (transgressive segregation), it is possible to determine whether the genes in the parents are in fact the same or different. In some instances, results of such studies imply that the same gene for Al tolerance is present in the different Al-tolerant genotypes being evaluated in this fashion because no progeny exhibiting less Al tolerance than the parents were found [41,42]. However, Camargo [36] reported that when BH1146 and
Atlas 66 were crossed and F2 progeny analyzed at an Al level at which both parents are tolerant, digenic segregation was observed, implying that these two highly Al-tolerant cultivars possess distinct Al tolerance genes that were both segregating in the F2 population. Thus, there appears to be some firm evidence that different genetic loci contribute to Al tolerance differences in wheat, but the number of such genes remains unknown.

An additional source of Al tolerance variation in wheat that could represent an additional layer of complexity is allelic variation within a given locus. It would seem surprising to find that significant levels of allelic variation could have evolved since the domestication of wheat. Indeed, molecular genetic studies have generally revealed that quite low levels of DNA sequence polymorphism exist in wheat. Nonetheless, allelic variation does exist for other traits, so it is not unreasonable to assume that such variation may extend to Al tolerance genes. Allelic variation for Al tolerance genes has been reported for both barley and maize, where multiple allele series of the same gene encode varying degrees of Al tolerance among cultivars [43,44]. In wheat this has not been definitively established, but it is interesting to note that the Al tolerance gene AltBH1 from the highly Al-tolerant cultivar BH1146 and Alt2, a gene from the less tolerant Chinese Spring, reside at roughly the same position on chromosome 4D [24,45]. We might suggest that these genes represent alternative alleles of a common locus, but we have only just begun to explore this issue.

In summary, significant levels of genetic variation for Al tolerance exist in wheat and have been exploited in breeding programs to improve productivity on acidic soils with chronic Al toxicity problems. Aluminum tolerance is not an intrinsic feature of wheat but rather is likely to have arisen by mutation during the course of its evolution, after a series of polyploid events resulted in the creation of its hexaploid genome. Extreme levels of Al tolerance in wheat can usually be traced back to a select few ancestors of Brazilian origin and appear to be under rather simple genetic control. This source of Al tolerance has been used worldwide to improve wheat production on acidic soils. However, the broad distribution of Al tolerance observed among wheat cultivars as a whole suggests that a simple genetic model does not adequately explain Al tolerance variation in this crop. This continuous variation is likely to be due to the presence of multiple genes that have evolved independently, multiple allele series for these genes, interactions between loci, or combinations of all of these factors.

4 MOLECULAR GENETICS AND MOLECULAR BIOLOGY OF ALUMINUM TOLERANCE

As we enter an era in which the tools of molecular biology present extraordinary opportunities to address questions in biology, many such opportunities also exist for exploring the genetic basis of Al tolerance. Obtaining answers to these ques-
tions is not only of interest for basic biological reasons but may have quite broad significance for crop improvement on acid soils. Over the past several years, a few studies involving molecular approaches to improve Al tolerance have been conducted.

This activity is not disconnected from the explosion of research focused on generating molecular maps of crop plants. An array of different methods for generating these maps has become available [46–49], and now the generation of such molecular maps is routine and, from a technical standpoint, not particularly demanding. As for other major crops, much effort has been directed at the generation of molecular maps of wheat (for example, see GrainGenes web site, http://wheat.pw.usda.gov/). From a practical standpoint, these maps have found their greatest application in the identification of molecular markers for genes encoding traits of agricultural importance. Even a cursory review of the current applied plant genetics literature will reveal the diversity of research efforts seeking to identify markers for genes involved in disease resistance, quality, and abiotic stress tolerance, including Al tolerance.

To date, two separate studies have identified molecular markers for Al tolerance genes in wheat. Riede and Anderson [24] identified marker loci for the gene $\text{Alt}_{BH}$, which confers a high degree of Al tolerance in the Brazilian wheat cultivar BH1146. Segregation for $\text{Alt}_{BH}$ was scored as a discrete Mendelian character by root hematoxylin staining of Al solution-grown recombinant inbred lines from the cross BH1146 × Anahuac. Single-gene control was indicated by the 1:1 segregation ratio and was confirmed with root growth measurements. Restriction fragment length polymorphism (RFLP) mapping located $\text{Alt}_{BH}$ on the long arm of chromosome 4D. The marker most tightly linked to $\text{Alt}_{BH}$ was the locus $\text{Xbcd}1230$, which was approximately 1 centimorgan (cM) from $\text{Alt}_{BH}$, whereas the marker locus $\text{Xcdo}1395$ was approximately 10 cM from $\text{Alt}_{BH}$. When Al tolerance segregation was treated as a metric variable rather than as a discrete variable using actual root growth data, $\text{Xbcd}1230$ accounted for 85% of the phenotypic variance for Al tolerance. Thus, $\text{Alt}_{BH}$ contributed virtually all of the Al tolerance to BH1146, with the residual variance presumably due to environmental effects and/or segregation for minor genes influencing root growth independent of Al.

In another study, Luo and Dvorak [45] used hematoxylin staining to map a gene conferring Al tolerance in the landrace Chinese Spring. Scored strictly as a Mendelian character, this gene (designated Alt2) was also mapped by RFLP analysis to the long arm of chromosome 4D, a location consistent with results of analyses of Al tolerance in Chinese Spring cytogenetic stocks [50,51]. Because Chinese Spring has less Al tolerance than BH1146, Alt2 is not the same gene as $\text{Alt}_{BH}$, but it may represent an alternative allele of the same locus that conditions less Al tolerance. This hypothesis is bolstered by the inference from hematoxylin staining results that each gene appears to confer Al tolerance by excluding Al from the root apex [24,45].
The most obvious use of such markers (particularly those identified for AlnH, a gene with potential importance to breeding programs) would appear to be as a tool for marker-assisted selection of Al tolerance. However, the adoption of molecular markers for this purpose may be of questionable value because other rapid, inexpensive, and simple methods for evaluating Al tolerance in wheat are available, as previously discussed, and have been used successfully by breeding programs to select for Al tolerance (summarized in Ref. 3). However, marker-assisted selection for Al tolerance may be justified by the preexistence of a marker-assisted selection program for other traits or when it would be cumbersome to undertake a specific selection program for Al tolerance because it might impede screening and selection for other important traits, such as seedling selection for disease resistance. Also, bioassays conducted on juvenile plants in nutrient solution culture or in soil media under controlled conditions do not have the full predictive value of mature plant performance in the field. A marker-assisted selection program might be developed to bypass these forms of selection and to apply selection pressure for other traits critical to acid soil tolerance, such as phosphorus use efficiency.

An additional use of such molecular markers will be to help resolve questions about Al tolerance gene diversity in wheat. As additional molecular mapping data become available, a more comprehensive picture of gene number versus allele diversity in this species will be acquired. Should mapping data ultimately reveal the presence of distinct Al tolerance loci among wheat cultivars, it may be possible to use the molecular markers to pyramid different Al tolerance genes in a single genotype and thereby obtain additive enhancement of Al tolerance. The potential for gene pyramiding to obtain increased Al tolerance can be inferred from some studies that have shown that backcross breeding, which is often used to transfer a single desired gene from one cultivar to another, may result in incomplete Al tolerance transfer from a tolerant cultivar to a sensitive one [40,41]. This suggests that Al tolerance genes may have an additive effect in certain instances that can be exploited to enhance Al tolerance.

Molecular mapping studies have provided additional scientific insight into more basic questions associated with Al tolerance. Within the last decade, it has been established that chromosome structure, and thus gene order, among related plant species, including the domesticated grasses, is conserved [52]. Because gene order is conserved among members of the domesticated grasses, cross-species comparative molecular mapping of Al tolerance genes can be used to address the question of interspecific Al tolerance gene conservation, i.e., do different species rely upon the same or different genes to obtain Al tolerance? Comparative mapping provides a means for answering this question. To date, limited data exist on chromosome locations of Al tolerance genes in other species, but hypotheses are beginning to form regarding interspecific Al tolerance gene diversity. For instance, Minella and Sorrells [53] used trisomic analysis to determine that a major
Al tolerance gene in barley, *Alp*, was located on chromosome 4. Because barley chromosome 4 is homeologous to the wheat group 4 chromosomes, this suggested the possibility that *Alp* and the wheat Al tolerance genes *AltBH* and *Alt2* on the long arm of wheat chromosome 4D are orthologous.

Recently, a study in one of our laboratories [54] identified molecular markers for *Alp*; this gene was found to reside on the long arm of barley chromosome 4, which is homeologous to the long arm of wheat chromosome 4D. Further, *Alp* was found to be linked to *Xcdo1395*, which is also linked to *AltBH* in wheat [24]. *Alp* was approximately 2 cM from *Xcdo1395*, and *AltBH* was reported to be approximately 10 cM from the same RFLP marker locus in wheat. This quantitative difference in linkage intensity could be due to an apparent chromosome rearrangement, positioning *Alp* and *Xcdo1395* closer to the centromere than *AltBH* and *Xcdo1395* are in wheat, thereby causing suppressed recombination between the two loci in barley. This conservation of linkage between *Xcdo1395* and both *AltBH* and *Alp* strongly indicates that these two Al tolerance genes are likely to represent orthologous loci and that independent mutations at this locus underlie natural variation for Al tolerance in both species. Additional mapping of Al tolerance genes has also been conducted in rye, where markers have been identified for major Al tolerance genes on rye chromosomes 6R and possibly 4R [55]. Interestingly, rye chromosome 4R has a segment syntenic with the Triticeae group 4 chromosomes [56], raising the possibility that in the tribe Triticeae—which includes wheat, barley, and rye—Al tolerance will consistently be found to be partly or wholly explained by parallel mutations in orthologous loci. Thus, gene discoveries in one species may accelerate gene discoveries in others.

Although the question of Al tolerance gene diversity is of basic interest, it also has broad practical implications for further genetic improvement in wheat and other species. If gene identity is found to be conserved across species, one may view the genes in different species as an extended allele series spanning species boundaries. This implies the possibility that if such a conserved Al tolerance gene can be cloned from a highly Al-tolerant plant and transferred intact into a less tolerant plant known to possess a less effective ortholog, the introduced donor gene could be expected to act as a new allele of this locus, resulting in a level of Al tolerance commensurate with the level conferred by the gene when present in the donor species. In contrast, if unique tolerance genes are identified in different species, their cloning would present the opportunity to pyramid these genes within any given crop by genetic engineering as a means to increase Al tolerance.

The isolation of an Al tolerance gene from wheat has been a goal of scientists for many years. Efforts to clone Al tolerance genes from wheat date back nearly a decade and first involved studies to identify the protein products of such genes. The identification of a protein can serve as a starting point for working backward to isolate the respective gene encoding it. In 1991, a number of independent groups reported on such attempts. Delhaize et al. [57] and Picton et al. [58] de-
scribed polypeptide differences in root apices of Al-tolerant versus Al-sensitive cultivars. Delhaize and coworkers used the Al-sensitive Egret and the Al-tolerant Carazinho, while Picton and coworkers used Warigal as their sensitive standard and the tolerant cultivar Waalt. Using two-dimensional (2-D) electrophoresis, each group identified constitutive differences in polypeptide profiles between the cultivars being compared in the absence of Al. Furthermore, they both reported that Al exposure induced polypeptide synthesis in both cultivars as well, including a few polypeptides preferentially induced in the Al-tolerant cultivars. The polypeptide differences present in the tolerant lines, but not the sensitive lines, were considered as possible Al tolerance gene products. However, when Delhaize and coworkers examined Al-tolerant versus Al-sensitive sister lines derived from a cross between Egret and Carazinho, none of the polypeptide differences present in Carazinho were consistently associated with the presence of Al tolerance or its absence, indicating that they are not encoded by the Al tolerance gene itself.

Similar studies were conducted by Ownby and Hruschka [59] and by Basu et al. [60]; however, one notable difference is that they actually attempted to partition the root tip polypeptides into microsomal (membrane-associated) and cytoplasmic fractions to obtain more specific information on the cellular locations of the polypeptides. As in the previous studies, various polypeptides were found to accumulate during Al stress, and in some cases differential expression between tolerant and sensitive cultivars was observed. Follow-up research by Cruz-Ortega and Ownby [61] classified one of the proteins that they had previously identified on 2-D gels as being induced under Al stress as similar to pathogenesis-related proteins, based on protein sequence data. However, because this polypeptide is induced in both Al-tolerant and Al-sensitive cultivars, it is unlikely to represent a true Al tolerance gene product. Taylor et al. [62] and Basu et al. [63] demonstrated that a 51-kDa polypeptide and a 23-kDa polypeptide, induced upon Al exposure in Al-tolerant wheat cultivars appear to cosegregate with the Al tolerance phenotype in segregating populations. The 23-kDa polypeptide is exuded by roots and has Al binding activity [63]. This is an interesting finding, but it remains to be seen whether the gene encoding this polypeptide is also linked genetically with Al tolerance segregation, which would strengthen the possibility that the polypeptide may indeed be an Al tolerance gene product. Thus, despite a number of attempts, a protein-based strategy for isolating a bona fide Al tolerance gene has not been successful. However, given the dramatic analytical improvements in protein analysis methods that have developed with the maturation of proteomics as a scientific discipline, such a strategy may eventually be fruitful.

In addition to protein-based studies, several attempts have been made to clone Al tolerance genes by molecular methods. This has included a number of studies that have approached the problem by searching for genes that exhibit increased expression upon Al exposure. The first of these attempts to be reported was by Snowden and Gardner [64]. Using differential complementary DNA
(cDNA) screening of a root tip cDNA library from Al-stressed roots of the Al-sensitive cultivar Warigal, they isolated five cDNAs representing genes whose expression is induced by Al exposure. Constitutive expression of four of the five genes in the absence of Al was higher in the Al-tolerant cultivar Waalt than in Warigal. Interestingly, four of the five genes exhibited reduced levels of expression in Waalt when exposed to nontoxic levels of Al, whereas when toxic levels were used, the same four genes exhibited an increase in transcript abundance. Two of the cDNAs exhibited sequence homology to other genes; one was similar to metallothioneins, and the other encoded the enzyme phenylalanine ammonia lyase [64]. Later research by the same group identified two additional genes whose expression is increased upon Al exposure, one of which was similar to asparagine synthetase and one similar to Bowman–Birk proteinase inhibitors [65]. Similarly, in follow-up research on their earlier protein studies, Cruz-Ortega et al. [66] identified a β-glucanase and a fimbrin-like gene that were each up-regulated in root tips by Al exposure; the fimbrin-like gene is interesting because it plays a role in cytoskeletal formation, and the cytoskeleton has been suggested to be affected by Al toxicity in cells [67]. Hamel and coworkers [68] isolated several Al-induced cDNAs from the root tips of the Al-tolerant cultivar Atlas 66, including genes for peroxidase, cysteine proteinase, and oxalate oxidase.

Tests of the ability of certain of these genes to confer Al tolerance have been conducted by expressing these genes in plants and determining whether they confer an increased measure of Al tolerance. Ezaki and coworkers [69] reported on results of experiments in which they transformed Arabidopsis with a series of different Al-induced genes identified in several plant species, including one gene, a Bowman–Birk protease inhibitor, recovered from wheat [64]. Overexpression of this wheat gene was not found to increase Al tolerance of Arabidopsis plants. However, overexpression of a few of the other genes from other plant species did increase Al tolerance, although not dramatically and only across a narrow window of Al concentrations. Interestingly, two of these genes also conferred Al tolerance in yeast [70]. But it was suggested that this is due to an increase in basal stress tolerance and not to an increase in Al tolerance per se.

Thus, to date none of the genes recovered during the course of any of these molecular cloning efforts is likely to be a bona fide Al tolerance gene. Perhaps this is due to the fact that if one looks at the physiological mechanism of Al tolerance in wheat (Al-inducible malate release from the root apex), the response is induced within minutes of exposure to Al [71]. This suggests that the genes that encode the cellular machinery necessary for the Al tolerance response are constitutively expressed but that the mechanism of Al tolerance that this machinery encodes is rapidly activated at the biochemical level upon perception of Al. Therefore, Al tolerance genes in wheat and perhaps other plants may not actually exhibit induced expression at the molecular level, so differential screening methods that have been widely used in the aforementioned studies may not be appropriate for Al tolerance.
gene isolation. Nonetheless, some of the genes that have been identified in this fashion may play a role in cellular adaptation associated with the AI tolerance response itself; presumably the efflux of large amounts of malate from root tips could cause metabolic changes for which the cells would need to compensate.

Perhaps it is unfortunate that wheat has served as such a useful model for genetic and physiological research on AI tolerance because its polyploidy and large genome make it difficult to make the subsequent transition from these types of studies to complementary molecular biological research aimed at isolating AI tolerance genes. However, in the future it may be possible to undertake AI tolerance gene cloning efforts in a diploid relative of wheat with a small genome, such as rice (Oryza sativa L.), that is amenable to certain methods such as positional cloning and then use the resultant cloned genes to recover wheat homologs through traditional molecular methods. It therefore seems inevitable that within the next 3 to 4 years, AI tolerance genes from wheat and other plant species will be isolated, which will provide new insights into our understanding of this important trait and will offer novel opportunities to improve the productivity of crops grown on acid soils.

REFERENCES


Managing Soil Acidification Through Crop Rotations in Southern Australia

David R. Coventry and Alireza Farhoodi
Adelaide University, Roseworthy Campus, Adelaide, Australia
Ren-kou Xu
Chinese Academy of Sciences, Nanjing, P.R. China

1 INTRODUCTION

Wheat-based farming is the dominant production system in the 250- to 600-mm rainfall areas in Australia. This type of farming may use a pasture–ley, a phase system, or a continuously cropped system [1]. The ley system has short annual sequences of cereal crops separated with either short or long periods of legume-based pasture. With the phase system, the crop sequence is longer and can include pulse and oilseed crops as well as the cereals. Whatever the sequence of crops and pasture, the overarching farm objective is to provide an appropriate soil environment so that profitability is ensured without negatively affecting long-term sustainability. Farmers seldom follow strict rotations; rather, they develop flexible crop and pasture sequences based on rules that account for short-term goals and long-term environmental considerations. The rotations used must ultimately be consistent with providing a base for nitrogen and phosphorus fertility, an adequate soil structure associated with maintaining organic matter, and disease, pest, and
weed management. In all cropping regions there has been a trend toward increasing the cropping component in the rotation, assisted by reduced tillage systems, more retention of crop residues, and also an increase in nitrogen fertilizer use.

Soil acidification is recognized as a serious form of land degradation associated with crop rotations. In southern Australia, the acidification in farming systems that use rotations of crops and pastures is well studied, particularly in higher rainfall areas. In these crop rotations, the N cycle and C cycle contribute most to the acid input [2,3]. Application of lime is the main management option used for correcting the acidity caused by acidification. Although lime can change the chemistry of the top 5 to 8 cm of the soil and provide immediate benefits to crop production, it is also important that the crop–pasture rotation is managed so that further acid addition to the soil is minimized. In particular, attention has to be given to the way nitrogen and carbon are managed within the crop rotation.

What is clear from studies on acidification occurring in crop rotations is that much of the accelerated acidification is associated with nitrogen inputs into the farming system in excess of the needs of the plant [4,5]. Depending on the growing season rainfall, a 4 to 5 ha\(^{-1}\) wheat crop requires about 200 to 250 kg available N ha\(^{-1}\) to satisfy herbage and grain needs [6]. The primary source of mineral N available for supplying the N for such a crop is the soil. In a given year, a small portion (about 2%) of organic N in soil is mineralized from soil organic matter, contributing mineral N amounts of 100 to 200 kg ha\(^{-1}\) [7,8]. Further, the quantity of N\(_2\) fixed per legume year in the rotation can be about 100 kg N ha\(^{-1}\) [3,9]. However, in many situations in the crop rotation, the supply of mineral N from the soil may be insufficient to meet crop N needs, and thus fertilizer N is added to the system [10]. The ongoing problem faced by farm managers in making decisions about N requirements is ensuring that the N required for obtaining targeted grain or forage yield and protein levels is matched with the supply of N.

Acidification of soil can also result from addition of carbon acids as part of the return of organic materials to the soil and from the export of organic anions in products [11,12]. Obviously, these acidifying inputs, as well as inputs associated with optimizing crop N nutrition, are essential in maintaining productive, stable, and economic crop rotation farming systems. Therefore, an objective of acidification studies to date has been the understanding of the fluxes of both nitrogen and carbon in the soil and plant materials so that management strategies are developed that minimize soil acidification. In this chapter, we examine the agronomic management options available for use in crop rotations in southern Australia for minimizing soil acidification. These may be in addition to, but also associated with, lime use and the use of acidity-tolerant cultivars.

2 SOIL ACIDITY IN CROPPING AREAS

Acid soils are common in some parts of the sheep–wheat production areas in the southeastern and southwestern regions of Australia [13,14]. The extent of soil
acidity (pH measure) prior to the clearing of the land for agriculture was influenced by the annual rainfall and the different clay mineralogy of the soil parent material (which influences the buffering capacity of the soil). The extent to which soil acidification has lowered the pH in these areas since land clearing is similarly influenced by these factors, as well as the years since land clearing and the proportion of legumes in the rotation in that time [15].

The native vegetation prior to land clearing was dominated by deep-rooted, perennial species. With this vegetation mostly cleared, the replacement vegetation was mostly shallow-rooted annual pastures and crops. With this change, more water has drained in the soil profile. The rates of acidification are generally more pronounced in the higher rainfall areas, and soils with pH values in the range 4.8–5.5 (CaCl₂) are likely to be more susceptible to rapid acidification [16,17].

The higher rainfall cropping zones within Australia are the areas with an annual rainfall greater than 500 mm. There is extensive evidence of accelerated acidification affecting soils in higher rainfall cropping areas in northeastern Victoria and southern New South Wales [14,18]. These areas frequently experience deep drainage of water below the influence of plant roots [19]. The medium rainfall cropping zones have an annual rainfall between 400 and 500 mm. In Western Australia, acidification is affecting the medium rainfall cropping areas with sand over clay and sandplain soils [20,21]. In the medium rainfall cropping zone in Victoria, New South Wales and South Australia, there is evidence that soil pH has declined with crop-based farming, although there is only preliminary evidence that induced soil acidity is affecting crop production [22–24]. Finally, in the semiarid cropping regions (250 to 400 mm rainfall), acidity is not usually a problem, although in New South Wales some changes associated with the introduction of crop practices have been identified as affecting soil pH [25]. In contrast to the higher rainfall cropping zones, it is unlikely that the medium and semiarid rainfall areas would have regular deep drainage of soil water.

The poor productivity of plants grown in acidic soils can be due to combinations of soil-related toxicities (Al, Mn, H⁺) as well as deficiencies of essential nutrients (P, Ca, Mg, Mo, Zn). The correct diagnosis of the major limitations associated with acidity is important because crop yields on different acid soils can be low for different reasons [26]. The relatively high concentration of Al³⁺ in the soil solution is one of the main characteristics of strongly acidic soils and depends on many soil factors, including the predominant clay minerals, the organic matter content, and concentrations of other anions [27,28]. The Al³⁺ produced by the dissolution of clay minerals under acidic conditions can displace exchangeable cations from clay and other charged colloids. The chemical reduction of Mn is also augmented under low-pH conditions and therefore toxic concentrations of Mn²⁺ can develop in some acidic soils [29].

The buffer capacity of the soil directly influences soil acidity, with various inorganic soil components as well as organic matter being the most important materials in establishing pH buffer capacity [30]. The buffering capacity of the inor-
ganic soil components is related to both the permanent lattice charge and the pH-dependent charge [31]. With soil organic matter, the pH-dependent charge is due to the dissociation of carboxylic (stronger acids) and phenolic (weaker acids) groups [32,33]. Aluminum can be associated with soil organic matter, with strong Al–organic complexes such as with fulvic acid and citric acid, which are nontoxic to plants [34,35].

The long-term effects of soil acidification on soil properties include (1) a reduction in the soil cation exchange capacity (CEC) and an associated loss of ability of the soil to store reserves of nutrient cations, (2) accelerated mineral degradation with increased concentrations of Al\(^{3+}\), and (3) reduced soil biological activity [11]. Knowledge of the rates of acid addition and the chemical behavior of the acidity components is important as this provides the basis for agronomic management strategies for minimizing acid input in crop rotations.

3 ACIDITY IMPACTS ON CROP PRODUCTION

Lime use has been widely recommended for wheat-based farming where the soils are strongly acidic, particularly in the higher rainfall cropping areas [18,20,36]. In most situations where the soil pH was less than 4.7 (CaCl\(_2\) extraction), yield responses of the order of 20–100% with wheat have been obtained after liming the soil. The evidence from a wide range of sites with different field crops, including barley and canola, both known to be acid-sensitive species, and subterranean clover, is that lime use has given consistent yield responses [18]. These responses to lime application can be due to the correction of a number of the deficiencies or toxicities of acidic soils, although the reduction in soil Al\(^{3+}\) concentration is thought to be the most likely reason for crop yield improvement [37,38]. The benefits of using cultivar tolerance to avoid potential harmful effects of acidity have also been shown in situations where the soil acidity level is severe, as well as where the acidity is less severe (pH > 4.7–5.0). It is an easy management option to use acid-tolerant species or cultivars as the choice of crop in cropping rotations. Another advantage cropping enterprises have for managing acidity is the ease with which the lime can be incorporated within the top 5–8 cm horizon with soil cultivation. Thus, it is possible with regular lime use and time (and subsequent movement of the lime effect in the soil) to influence soil pH up to 15–20 cm depth [39,40]. In such situations, it should be possible to ameliorate or avoid the development of subsoil acidity.

In the cropping regions where the soils are acidic but where there are more variable or seasonally dependent responses to lime application (e.g., medium rainfall zones), there is a need for matching of lime inputs to a target pH or at least application of enough lime to offset ongoing acidification. In these areas, similarly to the higher rainfall areas, the lime applied must be related to some measure of agricultural production or a target pH that is based on changes in soil chemistry.
An optimal liming program should not only reduce plant-available Al and Mn concentrations to levels that allow optimal production of a particular crop but also ensure adequate levels of plant available Ca and Mg and create conditions conducive to beneficial soil fauna [41].

In some situations, negative effects associated with high applications of lime have been reported. For example, decreases in wheat yields can occur due to pH effects on disease incidence [42], and in some areas in South Australia the inducement of Mn deficiency may negate any positive yield response to lime, particularly in subterranean clover [43].

4 ACIDIFICATION PROCESSES

Soil acidification is the process in which a decrease in pH is the product of the change in $\text{H}^+$ and the pH buffering capacity of the soil [5]. In natural ecosystems, soil acidification generally occurs over a time scale of thousands of years, but under agricultural production it can occur over a time scale of decades [4,44]. If only rainfall is considered as an acid promoter in a closed natural ecosystem, the $\text{H}^+$ flux in a 1000-mm annual rainfall situation at pH 5.0 would be about 0.1 kmol H$^+$ ha$^{-1}$ year$^{-1}$ [45]. However, in wheat-based crop rotations in southern Australia, the rates of acidification can be 0.16 to 3.6 kmol H$^+$ ha$^{-1}$ year$^{-1}$ for pastures [46–49] and 1.0 to 7.5 kmol H$^+$ ha$^{-1}$ year$^{-1}$ for cereal-legume rotations [2,20,47,48,50,51]. The overall rate of acidification is dependent on the initial soil pH and buffering capacity, the time period involved, and the particular management system [17]. The N and C cycles contribute most to the acid and alkaline reactions in these rotations, with the processes involved in the generation of $\text{H}^+$, $\text{OH}^-$, and organic anions occurring independently in the soil and plant system [3–5,52,53]. The understanding of these N and C cycle processes is important as they provide background for development of nonacidifying management strategies.

Incomplete cycling of N in soils under crop-rotation management has been identified as a major cause of increasing acidity. Almost all the nitrogen in biological ecosystems exists as organic N compounds (R-NH$_3$). Given that R-NH$_3$ is the ecosystem N sink/source (the reference state for nitrogen), the addition of NH$_4^+$ makes the equilibrium of the reaction (R-OH + NH$_4^+$ $\rightarrow$ R-NH$_2$ + H$_2$O + H$^+$) shift toward the production of R-NH$_2$, and this process produces H$^+$. The production of NO$_3^-$ resulting from nitrification and its accumulation in soil releases H$^+$, and the loss of NO$_3^-$ accompanied by base cations leaves H$^+$ in the system. In a similar way, the addition of NO$_3^-$ makes the equilibrium of the reaction (R-OH + NO$_3^-$ + H$^+$ $\rightarrow$ R-NH$_2$ + 2O$_2$) shift toward the production of R-NH$_2$, and this process consumes H$^+$ (an alkaline reaction). The production of NH$_4^+$ from R-NH$_2$ mineralization also consumes H$^+$, so its accumulation is an alkaline reaction, and the loss of NH$_4^+$ (export) is likewise an alkaline reaction [11]. The combined
ammonification and nitrification of R-NH\(_2\) (including urea) generates 1 mole of protons for every mole of N transformed, and denitrification then can consume the protons (see Fig. 1). The ammonia volatilization process generates protons.

In a closed system where there is no net gain or loss of N associated with these N soil processes, no net generation of H\(^+\) ions occurs \([52,54]\). However, in a crop-rotation practice, an imbalance in the amounts of N entering and leaving the soil system does occur, and this can lead to permanent soil acidification. This imbalance is due to the requirement to improve the productivity of soils, and this is done through increasing the plant available pool of N either by stimulating biological N\(_2\) fixation or by the application of N fertilizers. The use of ammonia-based fertilizers, such as monoammonium phosphate and diammonium phosphate, that are frequently applied with the seed at sowing causes a net addition of acidity as they generate 2 or 1.5 moles of protons, respectively, for every mole of N, resulting in an excess balance of protons. Net acid addition can also result from the leaching and loss of NO\(_3\) from this cycle. When NO\(_3\) and basic cations leach from the rooting zone of the soil, there is a net cumulative H\(^+\) production in the soil of one H\(^+\) for every NO\(_3\) ion leached \([5,45,52]\). This results in permanent soil acidification in the zone where the nitrification occurs. Thus, amounts of acidity entering and staying in the soil system depend on the relative magnitudes of these N cycling processes.

The N transformation processes are soil induced, but the N cycle also involves plant-induced processes that contribute acidity and alkalinity to the soil.

**FIGURE 1** Nitrogen transformation processes that produce and consume acidity in soils.
The uptake and assimilation of N as NH$_4^+$ or N$_2$ into legume nodules lead to H$^+$ ion extrusion into the rhizosphere soil. The uptake of N as NO$_3^-$ by plants results in the generation of OH$^-$ and provides a balance to the H$^+$-producing processes.

Processes associated with the C cycle also contribute acidity and alkalinity, with organic anions being either removed in agricultural products or returned to the soil as plant residue or animal excreta [4,55]. The organic anions are alkalis on the assumption of conversion to undissociated acids. If the organic anions added back to the soil associate with protons to form undissociated organic acids, there is no net change in acidity. In fact, because organic acids such as carboxylic acid and phenolic acid are weak acids, there is always some part of these organic acids that dissociates to release H$^+$. This process increases the size of the soil H$^+$ pool, and thus soil acidity increases. If these reduced C compounds are then decomposed through respiration, this acidity is neutralized. However, the contribution of this process to soil acidity mainly depends on the nature of organic acids and the environment pH, and usually the decomposition of organic acid groups is slow compared with the dissociation process, so the outcome is an increase in acidity [56].

These H$^+$ balancing processes are spatially compartmentalized between the soil and the plant and are linked through the plant uptake of highly mobile NO$_3^-$ and the return of organic N to the soil. A crop or pasture may remove alkalinity from the bulk of the soil during the growing season and partially recycle this alkalinity to the soil surface when the crop residues are retained. Therefore, acidification of soils is likely to be separated temporally as well as spatially because of this compartmentalization of acidifying and alkalizing processes between soil and plant [11]. In some years, the net result will be that the soil is alkalizing, and in others years it will be strongly acidifying. For example, in the long-term study undertaken at Wagga Wagga (rainfall 540 mm), the first wheat crops in a wheat-dominated rotations were alkaline, subsequent wheat crops were mildly acidifying, and pastures in these rotations were strongly acidifying. The overall trend with time for the soil volume in this experiment was acidic [3]. In this study, most of the N leached below 30 cm was recovered within the same or the subsequent years, but drainage events did occur. Drainage losses can be highly episodic and can occur in medium rainfall cropping regions and even in semiarid regions [57,58]. Agronomic solutions for reducing drainage below the rooting zone will not always be possible. Given that farmers in southern Australia have been using high rates of N fertilizer (80 to 120 kg N ha$^{-1}$) over the past decade, it is likely that soils are accumulating large amounts of mineral N [38,59] and also have a significant redistribution of NO$_3^-$ from the surface to depth. This uncoupling of the H$^+$ balance will result in stratification of acidification between soil layers. Thus, irrespective of the episodic drainage events, the net result is the accumulation of acidity in layers within the soil profile.
MANAGING SOIL ACIDIFICATION

5.1 Efficient Use of Soil Nitrogen and Water

The greatest scope for retarding acidification in the high and medium rainfall cropping areas is through more efficient use of soil nitrogen and water. The cropping season in southern Australia commences in autumn, when sufficient rainfall is available for establishing winter crops. The low temperatures in winter slow crop growth, but then crops grow rapidly in spring and mature in late spring or early summer. Although summer rainfall can occur, its effectiveness is negated by high evapotranspiration [60]. The inclusion of legumes (either pasture or crop legumes) in crop rotations in southern Australia is essential for maintaining soil organic matter, weed and pest management, and soil biodiversity [1]. A legume pasture annually adds from N₂ fixation about 25 kg mineral N per tonne of pasture dry matter (DM) produced [61]. Various management practices, such as winter cleaning or spray topping, are recommended in all cropping areas, particularly in the year prior to cropping, to promote pure legume swards [9,62,63]. This is done not only to optimize legume N₂ fixation but also to remove the pasture grasses that are alternative hosts to cereal root diseases, such as cereal cyst nematode and take-all. Similarly, a year of growing a crop legume can contribute high N inputs (20 kg mineral N per kg DM [64,65]). During the dry and warm summer and early autumns that are common in southern Australia, there is a buildup of mineral N from plant residues and soil organic N. In such situations, it is common that 70–100 kg mineral N ha⁻¹ can be stored in the soil profile in autumn (mainly in the NO₃⁻ form) [8]. Also, it has been shown that drainage can occur regularly in the regions where annual rainfall is greater than 500 mm [3,19,66]. This is the situation most likely to produce high rates of NO₃⁻ loss, particularly when the rainfall allows rapid recharging of the soil profile and subsequent drainage of the NO₃⁻ below the reach of plant roots. Drainage events are also likely to occur in the less than 500 mm rainfall regions, albeit at a much reduced frequency.

Given that movement of NO₃⁻ is linked to soil water movement, it is essential at this time, prior to the onset of winter rains, that the soil profile is managed so that a water deficit exists. The capacity to hold NO₃⁻ in the soil depends on rainfall as well as on soil hydraulic characteristics. Recharge typically ranges between an average of 20 to 40 mm in the semiarid areas and 60 to 100 mm in the higher rainfall areas [19]. If the pasture phase has been based on annual species, it is possible that the soil profile is relatively full following the dry summer months. Based on the estimates given by Whitfield [67] and Smith et al. [68], there is a potential capacity for the storage of water in the soil of about 100 mm (in a 1–3 m depth) at the beginning of the winter season. A way therefore to minimize opportunities for leaching of NO₃⁻ is to create water deficits, thus regenerating this soil storage capacity. This can be done by using either out-of-season crops/pastures or seasonal crops/pastures with active root systems that remove water from depths beyond the
roots of annual crops and pastures. For example, deep-rooted perennial pastures, such as alfalfa, cocksfoot, and phalaris, that actively grow through the dry summer months could be used as sinks for a few years accumulation of excess water [19]. Similarly, dryland crops such as grain sorghum can also use water stored deeper in the soil when grown in the summer months [69]. Passioura and Ridley [19] suggest that such management strategies could create a storage capacity for holding about 3 years worth of drainage beyond 1 m. In much of the southern Australian cropping zone, this storage could range from 1 to 5 years depending on seasonal rainfall.

Some forage crops or grass-based pasture may be used as an effective sink for nitrogen within the growing season [11,70]. However, with the crop rotations used in southern Australia, the usual practice is to try to utilize soil available N for improving crop production. The objective must be to maximize crop growth and root activity for the full extent of the growing season. An option is early sowing of crops in the autumn that could lead to more complete absorption of soil NO₃⁻ before it is leached below the root zone with heavy winter rains [11]. Within the growing season, crops with more vigorous development of roots (e.g., cereals and canola compared with legumes) may be preferred for their more effective utilization of seasonal rainfall. Helyar et al. [3] described a situation where most of the N that leached below 30 cm was recovered within the same or subsequent years. Angus [71] has shown that wheat is able to reach NO₃⁻ deep in the soil profile late in the growing season. In the study described by Helyar et al. [3], the N input was only from the biological N₂ fixation associated with the legume pasture in the rotation. This study did not include nitrogen input from fertilizer N and thus does not reflect the high-N regimes utilized in current crop rotations. As mentioned previously, long periods of legume-dominant pasture and higher soil N concentrations brought about by high-N fertilizer inputs (often greater than 100 kg N ha⁻¹ annually) would be expected to increase the reserves of N in the soil profile. Where flows of water do extend beyond the reach of the roots of annual plants, permanent acidification will result. The management of soil water to try to create net deficits is essential to optimize opportunities for capturing this soil N in either grain yield, protein, or forage.

An overall improvement in soil physical, chemical, and biological conditions that stimulate root activity and rooting depth will also increase the efficiency of NO₃⁻ utilization and restrict loss by leaching. There are some situations in which systems with high nitrogen use are not experiencing ongoing acidification [46]. Liming the soil does improve conditions for root elongation deeper in the soil profile, and the higher yields obtained reflect improved water use and N use efficiencies [72]. Soil improvement practices, such as deep ripping the soil to break a hard compacted layer, gypsum use to improve hard-setting surface problems, and a reduction in tillage, can also improve yields on acidic soils [73–75]. Appropriate crop rotation not only improves the soil N fertility, especially where legumes are in-
volved, but also improves soil physical properties and reduces the incidence of insects, diseases, and weeds, thus improving the likelihood of optimizing crop water use efficiency [76]. Improved tillage strategies will be part of an appropriate agronomic package for management to minimize leaching losses. Maintaining crop residues (e.g., cereal straw) on the soil surface, in stubble-retained systems, may reduce the amount of N mineralized in comparison with a cultivated or stubble-incorporated system. But, overall, the use of no-till practices continuously will result in a concentration of nutrients in the surface of the soil and the alkalization of this layer, and this will potentially give a net acidification deeper in the soil. The main benefit of reduced tillage and stubble-retained crop management for minimizing acidification is that more cropping years in a crop–pasture rotation are possible. This provides the opportunity for more years in the rotation of crops where there may be a net annual alkalization of the soil [12].

5.2 Fertilizer Selection
Nitrogen fertilizer is now being used extensively to improve productivity in wheat and oilseed crops in most cropping regions in southern Australia. Many farmers, prior to establishing their crop, utilize soil tests to estimate the available soil N and the need for supplementary N input as N fertilizer. Frequently, N fertilizer is used in cereal and oilseed crops following pulse crops and pasture, which is an indication that the supply of N from soil sources is often much less than the anticipated demand from high-yielding crops. The choice of N fertilizer for farmers is based on price and method of application. The ammonium sulfate and phosphate, urea, and ammonium nitrate forms of N fertilizer are the least costly per unit of N. The form of N fertilizer strongly influences soil acidification rates [77,78]. There is an inevitable acidification caused by use of the ammonium forms (monoammonium phosphate and diammonium phosphate), even without leaching. There is also potential for acidification associated with NO₃⁻ leaching or loss in products for these fertilizers and nearly all other forms of N fertilizer (e.g., urea, ammonium nitrate, ammonium sulfate). When N fertilizer such as urea is nitrified, one net H⁺ ion is generated per N atom. These H⁺ ions can be neutralized only if the entire NO₃⁻ product is taken up and assimilated into plant organic N, and the subsequent plant organic anion that is produced upon decomposition of the plant residues neutralizes the remaining H⁺ ions in the soil. All the N has to return to the input form (NH₄⁺) for neutrality. If organic matter accumulates, the NH₄⁺-fertilized system can generate in excess of one H⁺ per atom of N, and this is in addition to the acidity produced from the leaching and removal of product. Thus, the use of N fertilizer has the potential not only to produce permanent acidity but also to affect the magnitude of acid input into the soil volume [79].

Given the requirement of farmers for a continuing yield productivity gain, the use of N fertilizer is probably going to increase in the future throughout the
crop rotation. To avoid accumulating mineral N in the soil, farmers should be planning to use the minimum N fertilizer needed for optimal growth, yield, and protein. Methods for establishing target crop yields, such as the approaches that define a potential yield based on growing season rainfall [80], can be used in determining a nitrogen budget. The N requirement of the crop can be estimated to correspond to the target yield. In most cropping regions in Australia, reasonable predictive soil tests for nitrogen are available [81,82]. These soil test figures can be used as an estimate of available soil N and, when matched against the predicted N demand by the crop, the amount of N fertilizer required for achieving the target yield and protein is known. However, despite recent improvements in predictions of both crop yield and minimum N fertilizer requirement, these predictions can be difficult at the farm level. This is because of the unpredictable climatic parameters that determine plant growth and soil N availability and also to some extent lack of knowledge about mechanisms governing N cycling.

The average response to N fertilizer is characterized by a plateau and a point of optimal return on investment that precedes the point of maximum yield response [83]. Once the maximum rate of N input is reached and with no further yield increase, there is inevitable NO₃⁻ accumulation and risk of leaching if there is an excess of available N for the requirements of the plant. To obtain maximum benefits from N fertilizers, it is important that they be applied at a time when the N is used most effectively by the plant. Nitrogen supply is needed early in the growth of a wheat crop in order to establish a high yield potential, mostly through the establishment of an adequate number of tillers and then fertile heads per plant. A common practice is to use the ammonium forms of N fertilizer with the seed at sowing to promote early crop vigor and tiller development. This is an acidifying practice. Deep placement of N fertilizer can be an effective strategy for increasing yield and for avoiding placing the fertilizer with the seed. Deep banding creates a zone of lower soil strength deeper in the soil and, combined with a concentration of nutrients placed at the base of this zone, encourages plant roots to grow to greater depth where there is often more soil moisture (and a higher chance of finding nutrients). Also, there is a need for a continuing supply of N to at least the boot stage in wheat to ensure the survival of tillers and the realization of the established yield potential. For this, certainly the best timing for application of N fertilizer is within the first 6 weeks after sowing.

In the southern Australian environment, where seasonal rainfall is variable and unfavorable seasons are often experienced, the regular use of N fertilizer involves a degree of risk of poor N use efficiency. Efficiency of N uptake in southern Australia varies widely from about 40 to 80%. The efficiency of N fertilizer with dryland crops can be improved by taking care with timing and placement of application [59]. Deferring or splitting the application allows some flexibility and reduces the risk. Some knowledge of the likelihood and extent of seasonal rains is required, and reasonably reliable predictive information can
now be obtained. Therefore, in favorable years, the rate of N can be increased, whereas in dry years it could be decreased or not applied at all. Topdressing as a tactical response to a favorable season, or a predicted rain event, can greatly increase yield and protein responses compared with using applications based on set recommendations [59]. In commercial practice, crop growers are faced with the need to obtain maximum yield return for the money spent on N fertilizer while also achieving the protein or oil requirements appropriate to various premium grades. Although the overall objective is to gain the most economic return from N fertilizer, the tailoring of the N fertilizer regime to match absorption capacity for N by the plant will also help to avoid high soil N levels and the risk of NO$_3^-$ accumulation or leaching.

The NO$_3^-$ fertilizers such as NaNO$_3$ and KNO$_3$ cause an alkaline outcome when taken up by plants but are not used in broad-scale cropping because of the high cost per unit N. Similarly, slow-releasing forms of N fertilizer (e.g., metal ammonium phosphate, guanylurea, polyolefin-coated fertilizers) and inhibitors of nitrification in soils [e.g., 2-chloro-6-(trichloromethyl)pyridine (N-Serve)] can also have positive effects by slowing acid input but are not used in crop rotations because of cost [53].

### 5.3 Plant Selection

Large responses in plant yields can be obtained by the use of crop and pasture plants with tolerance to acidity when compared with less tolerant plants grown within the acidic cropping areas in Australia. In some situations, even the species and variety with tolerance to acidity are affected by the extent of acidity [39,73,84]. The use of acid-tolerant crops and pastures is a low-cost input on farms that is easily adopted and can often change the cost/price ratio to values more favorable for initiating lime use. The choice of species or variety with better yield potential is obviously important for economic reasons. However, the choice of species or variety is also important as a management strategy to offset acidification, as plants tolerant to soil acidity are more likely to be using water through better root growth and be reaching more NO$_3^-$ deeper in the soil profile. The use of tolerant plants is important where subsoil acidity exists, particularly as the amelioration of acidity in the subsoil (i.e., below the soil volume where the lime has been incorporated) after liming is slow [39,85].

There is a risk, however, that reliance on crop choice alone, and not liming to correct acidity, will ultimately result in productivity losses as the soils acidify [84]. Reliance only on the use of acid-tolerant plants will be associated with the risk that acidification inputs will continue to some extent and, depending on the circumstances, this acidification may be hard to correct in the future. This situation often occurs in the high rainfall and nonarable pastoral areas in southern Aus-
tralia, where declines in pasture production are evident [86]. In these areas, there is a concern that with time there will be fewer pasture species with tolerance of acidity, particularly as the acidity develops at depth. An associated problem in these pastoral areas is the dependence on species such as subterranean clover that can persist at low pH, but their nodulation and growth may be adversely affected by the acidity [87]. Given the diversity of acidic soils, different acid-tolerant plants need to be identified and screened to ensure adaptation to the soil acidity complex. The issue should not be whether acidity tolerance is used but whether it is being used for the purpose of minimizing acid additions at the same time as increasing production.

The choice and balance of species and variety in the crop rotation are important, particularly in phase farming systems where a series of crops is alternated with a few years of pasture. The objectives of the rotations should include consideration of acidification influences such as water and NO$_3^-$ use in the soil profile and soil and plant C dynamics. For example, wheat grown following a break crop such as canola or Indian mustard can extract more subsoil N than wheat grown following wheat [88]. This may be due to increased water uptake, possibly because the root system of the wheat crop was healthier because of lack of pathogens or other biological or physical changes associated with the break crop. The uptake efficiency of N (net uptake in whole tops at maturity per unit of N applied) does vary between wheat varieties and is thought to be a function of the size and activity of the root system [89]. Thus, differences in N uptake efficiency between genotypes may also be important in the recovery of N in field-grown crops. Usually it is necessary to include pulse crops in any long sequence of crops. It is well established that some pulse crops, for example, lupins, provide a strongly acidifying event in the rotation [2,48].

Market considerations as well as climate and soil characteristics mostly influence the design and management of rotation sequences. However, for the purpose of minimizing soil acidification, consideration should be given to the intensity of cropping and crop choice in the rotation for targeting high efficiency of nutrient removal and water use. The objective for sustainability is to manage the crop sequence so that the influence of strongly acidifying years is minimized. Particular attention should be paid to minimizing the effects of acid addition in the last pasture year in phase rotations or in pulse years in a continuous crop sequence. The choice of perennial species in the pasture phase is therefore preferred because of the greater opportunity to exploit the storage capacity of the deep subsoil [8]. Alfalfa is a useful plant for this purpose, although its sensitivity to acidity may limit this option. In the cropping sequence, consideration can also be given to regenerating the water storage capacity of the soil and ensuring that less acid is retained in the soil by careful management of N supply and efficient plant use of N.
5.4 Tillage, Stubble Management, and Organic Matter Dynamics

Organic matter is vital to the structural stability of soil, is an important reservoir of nutrients, and is essential for maintaining soil biodiversity. However, the addition of organic matter to soil can result in increases or decreases in soil pH, depending on the influence that the addition has on the balance of the various processes that consume and release protons. In the temperate crop–pasture systems of Australia, the levels of organic matter are built up with successive years of legume-based pasture (accompanied by N$_2$ fixation), often approaching a steady state in soil organic C that is dependent on rainfall and soil type [1,90]. Improving organic matter results in a significant increase in both the size and rate of the soil C and N cycles, both of which contribute residual acidity to the soil [4,52].

The introduction of cropping following pasture and accompanied by either a fallow phase or cultivation prior to crop establishment can lead to increased nitrification rates [91]. Crop residues also contain significant amounts of N as organic anions in the stubble (e.g., 14 to 22 kg N ha$^{-1}$ [92,93]), which is lost to the atmosphere if this stubble is burned. Although stubble return is an obvious source of organic N for the soil, the organic content of the soil usually declines through cropping sequences irrespective of the crop used and method of tillage and stubble management [1,24,94,95]. For example, Slattery et al. [95] measured reductions in organic carbon in the 0 to 10 cm soil layer from about 15 to 11.5 g kg$^{-1}$ over a period of 15 years with continuous cropping. Such losses of organic matter and associated declines in CEC significantly reduce the capacity of the soil to buffer against declines in soil pH.

The crop–pasture ley rotations in combination with fallow breaks, which were commonly practiced in southern Australia during the period 1960–1990, have been implicated in the widespread acidification throughout many regions [3]. The use of multiple cultivation has led to an exploitation of the accumulated organic matter and an increase in the rate of nutrient cycling. However, during the period 1990–2000 there was a significant change in the management of soil in preparation for cropping. The practice of burning stubble to make sowing operations possible has diminished as sowing equipment for handling stubble at sowing has been developed. Although stubble may still be burned for pest, weed, and disease management purposes, generally farmers prefer to return crop residues to the soil in crop rotations. This may involve a stubble retention system, where the plant material lost as litter during crop growth and the stubble from the previous crop is retained on the soil surface, or a stubble incorporation system, where the stubble is cultivated within a plow layer. Whatever the stubble management practice, it is necessary to reduce the quantities of stubble remaining prior to sowing (relative to that available at harvest) and there will still be some associated loss of organic material from the soil system. Farmers also prefer now to minimize the number of
times the soil is cultivated. Many farmers opt for direct drill (only soil disturbance during the sowing operation) or zero till that has virtually no soil disturbance. The return of plant materials to soil has important implications for managing soil acidification.

An alkaline effect results initially from the return of plant materials containing organic anions to the soil surface. This return of organic anions to the surface balances, in theory, the acidifying effects caused by the previous ammonification and nitrification of organic-N compounds, where at least 1 mole of protons was produced and retained in the soil. This balancing of acidifying and alkalizing processes was the likely outcome in the study reported by Poss et al. [12] where wheat as a rotation crop contributed little to acidification. The assumptions given for that study are that the stubble from the wheat crop has remained on the field and that any NO$_3^-$ leached to depth in the soil has been taken up by root development. In such a crop year within a rotation, where only a few products escape the system, the acid additions should be mostly balanced with the organic anions as they are returned to the soil. In situations where there is more loss of crop residues and products from the system, residual acidity will remain in the soil. But practices such as stubble retention and minimum tillage would reduce and possibly balance this source of retained acid. However, in practice, these acid-producing and acid-consuming processes are spatially and temporally separated. The H$^+$ ion generating process of the soil and rhizosphere associated with the N cycle has occurred mostly deeper in the soil than at the soil surface or in the plow layer, where the OH$^-$ ion generating processes as part of the return and accumulation of organic N occur. As a consequence, there is likely to be some stratification of acidification in the soil and, with time, development of permanent acidity [11].

It is recognized that acidification also results when carbon acids are formed from the organic anions as soil organic matter accumulates. The pasture component in the crop–pasture rotation is essential for increasing soil organic matter. The pasture phase in the rotation certainly contributes more acidity resulting from organic matter accumulation than crops. Heenan et al. [90] showed that the proportion of acid added from organic matter accumulation and product removal increased from 20 to 36% as the proportion of pasture in the rotation increased from 33 to 67%. Half to two-thirds of this was due to organic matter accumulation. Even though organic matter can have a strongly acidifying effect in crop rotations, any reduction in organic matter to counter this acidification will be counterproductive to the cropping system [11]. Maintaining organic matter in crop rotations is essential for the structural stability of soil, but it also has benefits that assist with countering acidity. The weakly acidic functional groups on soil organic molecules act as conjugate acid–base pairs and make soil organic matter an effective buffer for pH change [96]. Organic matter decomposition also releases organic acids known to complex toxic forms of Al [34]. The organic matter has a CEC originating mostly from carboxylate (—COO$^-$) groups, and this proportion of the soil
CEC is important for maintaining plant nutrients. Thus, the maintenance of soil organic matter is required in a highly producing crop rotation.

5.5 Product Removal

Soil acidification also results from the removal of products that contain organic anions (alkalinity), with unneutralized $\text{H}^+$ ions remaining in the soil. The amount of organic anions in products varies greatly. The removal of products low in organic anions, such as cereal grain, is less acidifying than removal of products high in organic anions such as alfalfa hay; for example, starch-dominated cereal grain removes 5 to 10 cmol(−) kg$^{-1}$ compared with removal with alfalfa hay of 100 to 150 cmol(−) kg$^{-1}$ [11]. Some acid addition to the soil must be accepted as part of a commercial farm operation. There is a limited opportunity to reduce this in a cropping system as the grain removal is unavoidable, but the losses in grain contribute little to acid input [2]. However, losses associated with the burning of stubble are avoidable.

Acidification associated with pasture–livestock or forage hay (export) enterprises can be more substantial. With grazing enterprises, practices such as feeding conserved forages on paddocks from which the forage was removed, returning dung and urine waste products to the donor field, and fencing to minimize camping behavior are recommended [11]. The intensity of grazing is also an important consideration as heavier grazing can result in greater amounts of N mineralization and the potential for either more plant N uptake or soil N accumulation [97].

6 REQUIREMENT FOR PRODUCTIVITY GROWTH

In the temperate agricultural regions in Australia, soil acidification is a form of land degradation associated with highly productive agricultural systems. Acidification has been recognized to date in the higher rainfall crop rotation areas associated with high input–high output cropping systems. In these areas awareness exists (mostly among primary producers) that acidification is a major problem. Here liming is seen as an economic option, despite the high cost of lime and freight [36,98]. In the medium rainfall areas, there is only limited awareness of acidification as a form of land degradation. In all these cropping areas, it is possible to restrict acidification by use of management practices that minimize acid accumulation and do not limit productivity growth. Within the overall goals and objectives of the farmers, the following strategies should be considered to meet nonacidifying outcomes.

Nonacidifying systems involve the efficient use of soil N and water. In phase farming systems, deep-rooted perennial species should be considered for creating soil water deficits and thereby less opportunities for drainage. Crop
choice, rotation choice, and soil management must be integrated so that the development of vigorous root systems is achieved. There should be more precision in the use of N fertilizer to ensure optimal crop N-use fertility. Wherever possible, plant materials should be returned to the soil at the site of origin. No-till systems should be used as this allows the intensification of crop sequences in the rotation with more opportunity for effective use of soil N. Liming the soil will often be undertaken in association with these nonacidifying management practices. Soil testing and the use of models for determining optimal lime and N fertilizer rates should be part of this practice.

Crop production in the medium to high rainfall areas in Australia has experienced an ongoing productivity growth of about 2.5 to 3% during the past few decades [99]. Soil acidification is a form of land degradation that can be accelerated in seeking more productivity growth. However, the nonacidifying strategies given previously are entirely consistent with best practice farm management for realizing further productivity growth. The emphasis in this chapter has been on a specific farming system in defined areas within Australia. However, the principles for the development of nonacidifying farming systems have a much wider application. The rapidly increasing population of the world is forcing food crop production onto more marginal acidic soils. It has been predicted that world population will increase between 2000 and 2050 from 6 billion to 10 billion, with a requirement to maintain or increase the growth rate in production [100]. The outcome of increased farm productivity must be established as a consequence of the functioning of the total interactive agricultural, environment, and social system and should be based on an understanding of the interrelationship between the soil and plant system.

REFERENCES

61. MB Peoples, DF Herridge, JK Ladha. Biological nitrogen fixation; an efficient


76. RG French. Future productivity on our farmlands. Proceedings of the 4th Australian Agronomy Conference. La Trobe University, Bundoora, Victoria, Australia, 1987, pp 140–149.


1 INTRODUCTION

Acidification of forest soils is one of the major problems facing forestry throughout many regions in the world. The adverse properties brought about by acidification and encountered by trees are essentially the same as those faced by crop plants, i.e., low availability of base cations and high loading of Al on the soil cation exchange system [1]. However, the longevity of forest systems, where even in intensively managed plantations the rotation time may be in excess of 40 years and in more natural forests over 120 years, poses a number of specific problems. The aim of this chapter is not to discuss in depth the causes and effects of acidity on forest ecosystems, but rather to discuss the difficulties and implications of trying to manage soil acidity in forest soils.

2 CAUSES OF INCREASED ACIDITY IN FOREST SOILS

2.1 Naturally Occurring Acid Soils

Within any ecosystem soil acidification will occur when acidity-generating processes outweigh acidity-consuming processes [1]. In most nonmanaged ecosys-
tems, base cation depletion is balanced by (1) uptake into plant biomass, (2) leaching by vertical water flow, and (3) cation consumption and resupply by soil buffering and mineralization. In many temperate and tropical forest ecosystems, these processes have led to natural acidification of forest soils over a number of decades. In a review of calcium in terrestrial ecosystem processes [2], a number of examples of natural soil acidification have been described. In tropical forests, high soil acidity and Al toxicity are common [3]. In South American central lowlands, it was estimated that 43% of the land (350 million ha) is potential affected by Al toxicity (defined as >70% of the soil cation exchange capacity being occupied by Al). The high levels of soil acidity are a result of rapid decomposition of organic matter due to the high temperatures and high rainfall exceeding evaporation, leading to poor retention and leaching of base cations. In temperate spruce–fir forests of the eastern United States, precipitation in excess of evapotranspiration is thought to have produced highly acidified upper soil horizons. In these horizons, the pH is <3.2 and the base saturation less than 5% [4].

The high removal of base cations in tree biomass also leads to depletion of Ca and Mg in soils. Based on work of a number of authors [5–7], McLaughlin and Wimmer [2] describe a number of scenarios in which growth of forests leads to depletion of soil base cations. In an example of postglacial primary succession, the development of a forest community on base-rich, N-poor substrate results in increasingly high incorporation of base cations and N into the biomass and the soil organic matter. The nutrient storage in the organic matter helps to buffer against nutrient deficiencies. The system takes several hundred years to develop but results in more acidic forest soils with lower contents of base cations. The changes in soil Ca suggested by Ulrich [5] are supported by data on the removal of Ca from the soil in a 250-year-old primary succession sequence in Alaska [7]. After 250 years, 75% of the soil Ca was lost, but more significantly for managed forests, approximately 50% was lost after the first 100 years. McLaughlin and Wimmer [2] describe forest growth leading to three acidifying chemical processes:

1. Incorporation of Ca into woody biomass
2. Loss of Ca by increased leaching as H replaces Ca on cation exchange sites
3. Reduced availability of Ca due to Al antagonism

Van Breemen [8] suggested that soil development is strongly affected by tree vegetation type. Thus, growing forests are themselves a cause of soil acidity. In temperate regions, managed forests are mostly replanted forests or remnants of natural postglacial forests. Replanted forests have often been established on nutrient-poor soils unsuitable for agricultural production. Similarly, remnant forests are often on soils too poor or too inaccessible to warrant clearing for agri-
culture. The initial poor soil conditions exacerbate the acidifying effects of forest growth.

2.2 Acid Deposition

In Europe and North America, acid precipitation has greatly increased rates of soil acidification in forest ecosystems. The increased soil acidity is a result of both direct proton input and internal proton production during nitrogen turnover. The acidification of forest soils has a number of consequences for the physiology of trees and the element budget of ecosystems, which must be considered if soil acidification is to be ameliorated by liming.

The common symptoms of tree damage are Ca deficiency in the eastern United States [9] and Mg deficiency in central European forests [10,11]. In an attempt to evaluate the changes in nutrient supply to vegetation, Robarge and Johnson [12] divided nutrient pools into capacity factors and intensity factors. Capacity factors are slow-reacting pools. In the case of base cations, capacity factors are weatherable minerals, organic matter, cation exchange capacity, and base saturation [2]. Intensity factors include short-term variations in ratios of base cation to Al and changes in strong anion concentrations in the soil solution, as well as changes in factors affecting mass flow of nutrients in the soil solution, such as transpiration, and additional factors removing nutrients from vegetation, i.e., foliar leaching.

Increased soil acidity in forests has resulted in increased leaching rates of base cations and increased availability of Al. Whereas in forests in the northeastern United States most emphasis has been placed on the increased depletion of Ca from soils [13,14], in European forests depletion of both Ca and Mg is of major significance [1]. Joslin et al. [14] estimated rates of leaching of Ca in forests affected by acid deposition to be approximately double the natural leaching rates. In the northeastern United States, a decrease in nutrient supply capacity has been happening for the last 60 years [9]. This is evident as a decreased cation exchange capacity of the humus layer and reduced retention and availability of Ca in the humus layer [15]. For a number of sites in Germany, Ulrich [1] reported a loss of nutrient cations and a decrease in base saturation. McLaughlin and Wimmer [2] suggested that changes in intensity factors appear to be the primary effect of acid deposition in forest soils, which have been subject to depletion of nutrient supply capacity. Ratios of base cation to Al are lower in the mineral soils that in organic upper soil horizons, resulting in limited growth of roots in the mineral soil. Low base cation/Al ratios affect the uptake of both Ca and Mg by tree roots [16] and also lead to injury to roots [16,17]. A number of studies have shown reduced root penetration into deeper soil layers, leading to shallower root systems on acid soils [4,18,19].

In addition to the changes that have taken place in forest soils because of proton inputs, anthropogenic inputs have led to nitrogen and heavy metal accu-
mulation in forest ecosystems [20]. Many forest ecosystems in both Europe and North America have reached nitrogen saturation [21,22]. Nitrogen saturation is the point at which N input rates exceed rates of aboveground and belowground utilization [23]. Eutrophication can have a number of negative effects on ecosystems, such as changes in vegetation cover. However, N saturation can also have significant effects on processes associated with acidification. Loss of N in the form of NO₃ can greatly increase cation depletion and mobilization of Al. In addition, in Europe, large areas of groundwater used for extraction of drinking water are under afforested areas [20].

3 LIMING FOREST SOILS

3.1 Liming Materials

In many countries in Europe, liming has been used as a method to counteract the effects of acid deposition [24–26]. Liming has been carried out with two primary aims, either to reverse soil acidification or to prevent further acidification (compensatory liming). In both cases, lime is applied to the surface humus layer. Only after trees have been cleared from the site is deep incorporation of lime into the soil possible. For compensatory liming, an amount of lime added is sufficient to neutralize the estimated proton input. For reversal of soil acidification, an amount of lime in excess of the estimated proton input is added. Most trials or liming measures have been carried out using calcite (CaCO₃) or dolomite [CaMg(CO₃)₂] mainly in a ground or half-sintered form (Table 1). For higher additions of Mg, kieserite (MgSO₄) has often been used. The rates of addition vary between 50 and 8000 kg ha⁻¹ but most commonly between 2000 and 5000 kg ha⁻¹.

The buffering of protons by calcite and dolomite occurs in two steps [27].

**Calcite**

\[
\text{Step 1: } \text{CaCO}_3 + H^+ \rightarrow \text{HCO}_3^- + \text{Ca}^{2+} \\
\text{Step 2: } \text{HCO}_3^- + H^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{CaCO}_3 + 2H^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}
\]

**Dolomite**

\[
\text{Step 1: } \text{CaMg(CO}_3)_2 + 2H^+ \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} + \text{Mg}^{2+} \\
\text{Step 2: } 2\text{HCO}_3^- + 2H^+ \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \\
\text{CaMg(CO}_3)_2 + 4H^+ \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_2 + 2\text{H}_2\text{O}
\]

The two dissolution steps as shown in the preceding equations buffer at different pH ranges. The buffering range for the step 1 is pH 8 to 6.5, whereas for step 2 it is 7 to 4.5 [28]. The mobile buffer substance is HCO₃⁻, which extends the deacidification front down the soil profile with the seepage water.
<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Liming material</th>
<th>Amount added (kg ha(^{-1}))</th>
<th>Effect</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fagne de Chimay, Belgium</td>
<td>1989</td>
<td>Calcite</td>
<td>50 to 8000</td>
<td>Increase of 0.16 pH units per t CaCO(_3) ha(^{-1}) applied</td>
<td>31</td>
</tr>
<tr>
<td>Hils, Germany</td>
<td>1982</td>
<td>Calcite</td>
<td>7000</td>
<td>Increase in pH from 3.8 to 4.2</td>
<td>32</td>
</tr>
<tr>
<td>Kahleberg, Germany</td>
<td>1985</td>
<td>Dolomite (50% CaCO(_3), 30% MgCO(_3))</td>
<td>~3000</td>
<td>Increase in pH by 0.3 unit</td>
<td>33</td>
</tr>
<tr>
<td>Prüm, Germany</td>
<td>1985</td>
<td>Dolomite liquid suspension</td>
<td>3000</td>
<td>Increase in pH from 2.5 to 3.8</td>
<td>34</td>
</tr>
<tr>
<td>Eggegebirge, Germany</td>
<td>1985</td>
<td>Calcite</td>
<td>3000</td>
<td>Increase in pH from 3.3 to 5.5</td>
<td>35</td>
</tr>
<tr>
<td>Grunewald, Germany</td>
<td>1986</td>
<td>Calcite/dolomite</td>
<td>6100</td>
<td>Increase in pH from 3.8 to 6.4</td>
<td>36</td>
</tr>
<tr>
<td>Höglwald, Germany</td>
<td>1984 to 1990</td>
<td>Dolomite</td>
<td>4000</td>
<td>Increase in pH from 3.8 to 6.4</td>
<td>27</td>
</tr>
<tr>
<td>Åseda, Sweden</td>
<td>1977</td>
<td>Calcite</td>
<td>5000</td>
<td>Increase in pH from 3.9 to 4.8</td>
<td>37</td>
</tr>
<tr>
<td>Norrliden, Sweden</td>
<td>1971</td>
<td>Calcite</td>
<td>5000</td>
<td>Increase in pH from 4.0 to 4.5</td>
<td>37</td>
</tr>
<tr>
<td>Several sites in Finland</td>
<td>1959 to 1962, relimed 1979 to 1982</td>
<td>Calcite</td>
<td>2000</td>
<td>Increase in pH from 4.2 to 5.6</td>
<td>38</td>
</tr>
<tr>
<td>Susquehannock, Pennsylvania</td>
<td>1985</td>
<td>Dolomite (12% Mg)</td>
<td>2240</td>
<td>Increase in pH from 3.8 to 5.4</td>
<td>39</td>
</tr>
</tbody>
</table>
The rates of dissolution will depend upon both the liming material properties, such as the grain size, and the relative amounts of calcite and dolomite. In addition, the rate of dissolution will be affected by a large number of site factors, including

1. The acidity of the soil
2. Acid deposition
3. Soil temperature
4. CO₂ partial pressure of the soil air
5. Removal of the dissolution products with the seepage water

Except in soils with high porosity, lime particles are generally not translocated with the seepage water, and movement into deeper soil layers is dependent upon incorporation by earthworms [27].

3.2 Liming Trials

In Germany, liming was used in forests in the 1950s and 1960s to increase N turnover and change the humus from a mor to a mull type [24]. The objective of the treatments was to increase the biological activity in disturbed topsoil layers on acid soils and thereby release nutrients stored in the humus layer. This liming was often combined with P fertilization. From these trials, much can be learned about the long-term effects of lime application to the forest ecosystems. Details of many of these studies are given in Huettl and Zoettl [24]. Between 1953 and 1965, more than 100,000 ha of forestland was limed [29]. In 1983, Aldinger [30] investigated the effects of liming carried out in the 1960s and 1970s as a measure to counteract the effects of soil acidification. In these trials, ground limestone was applied at a rate of 2500 to 3000 kg ha⁻¹. In 50 limed *Picea abies* (Norway spruce) and *Abies alba* (silver fir) stands, which had shown symptoms of a new type of forest decline since the late 1970s, a positive effect of lime was found in that the pH of the humus layer was increased. The effect of liming on soil pH of a number of other sites is shown in Table 1. At all sites, lime application resulted in an increase in soil pH. Only small changes were shown at the Fagne de Chimay site, but the change in soil pHe was estimated only 1 year after application [31]. There is, however, no clear relationship between the amount of lime applied and the change in pH.

As already discussed, the rate of dissolution of lime is dependent upon a number of factors. Kreutzer [27] estimated the rates of dissolution at 4000 kg ha⁻¹ dolomite application at the Höglwald site and found complete dissolution 6 years after application, where the decrease in carbonate could be described by an exponential equation with a half-time of about 13 months. However, even when sufficient time for dissolution of lime had elapsed between application and sampling, it is noticeable that the changes in pH were primarily in the upper (organic) soil layer (Table 2). Because of the different soils sampled at these sites, soil depth in...
cm does not always represent a similar physical soil layer; however, a general trend can be seen in that pH changes below 10 to 15 cm are absent or small.

The longer term liming trials also allow estimation of the effects of liming on forest health over a time period in which effects could be expected. In the trials investigated by Aldinger [30], the pH of the humus layer was increased, but the most common symptom of forest decline, needle loss, was not reduced. Similarly, little improvement in tree health was found in limed and fertilized Black Forest stands [40] or in limed stands in northern Bavaria [41]. In their review of a large number of liming trials, Huettl and Zoettl [24] drew the conclusion that addition of CaCO₃ alone is insufficient to improve the nutrition, growth, or vitality of trees.

In sites in the northern Black Forest investigated by Aldinger [30], it was shown in subsequent work [42] that a number of soil parameters, such as cation exchange capacity, base saturation, and exchangeable Ca (calcite application) and Mg (dolomite application), were increased. This change resulted in higher Ca contents in needles but lower levels of K in needles. The decrease in K concentration in needles was attributed to Ca inhibition of K uptake by the roots. Further, Huettl and Zoettl [24] suggested that this effect may not be unique to the K-poor soils of southern Germany. In an appraisal of 96 liming trials in Finland, Derome et al. [43] found that growth decreased by 3% in pine and 10% in spruce stands. Similarly, in Swedish liming trials, a decrease in growth was found in Scots pine and Norway spruce [44].

Thus, the conclusion is drawn that only lime materials that contain Mg will lead to revitalization of tree health [24]. In numerous studies, addition of Mg as either dolomite or highly available kieserite (MgSO₄) to trees showing decline symptoms rapidly resulted in a regreening of needles [24,45]. Addition of Mg-containing liming materials has increased growth and vitality of not only conifer-

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil layer defined</th>
<th>pH change</th>
<th>Soil layer defined</th>
<th>pH change</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kahleberg, Germany</td>
<td>0 to 30 cm</td>
<td>3.7 to 4.3</td>
<td>30 to 60 cm</td>
<td>None</td>
<td>33</td>
</tr>
<tr>
<td>Eggegebirge, Germany</td>
<td>0 horizon</td>
<td>2.5 to 3.8</td>
<td>A horizon</td>
<td>None</td>
<td>35</td>
</tr>
<tr>
<td>Grunewald, Germany</td>
<td>0 to 10 cm</td>
<td>3.3 to 4.1</td>
<td>&gt;10 cm</td>
<td>None</td>
<td>36</td>
</tr>
<tr>
<td>Höglwald, Germany</td>
<td>Oh-layer</td>
<td>2.8 to 4.4</td>
<td>7 cm</td>
<td>None</td>
<td>27</td>
</tr>
<tr>
<td>Åseda, Sweden</td>
<td>Organic layer</td>
<td>4.0 to 4.8</td>
<td>0 to 10 cm</td>
<td>4.6 to 4.7</td>
<td>37</td>
</tr>
<tr>
<td>Farabol, Sweden</td>
<td>Organic layer</td>
<td>4.0 to 6.4</td>
<td>0 to 10 cm</td>
<td>4.2 to 4.7</td>
<td>37</td>
</tr>
<tr>
<td>Färnhol, Sweden</td>
<td>Organic layer</td>
<td>4.1 to 5.9</td>
<td>0 to 10 cm</td>
<td>4.6 to 4.8</td>
<td>37</td>
</tr>
<tr>
<td>Several sites in Finland</td>
<td>Upper humus</td>
<td>4.2 to 5.6</td>
<td>Eluvial layer</td>
<td>3.8 to 4.1</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Lower humus</td>
<td>3.4 to 4.9</td>
<td>Illuvial layer</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Susquehannock, Pennsylvania</td>
<td>0 to 5 cm</td>
<td>3.8 to 5.4</td>
<td>10 to 15 cm</td>
<td>4.1 to 4.5</td>
<td>39</td>
</tr>
</tbody>
</table>
ous stands in Germany [24,45] but also sugar maple (*Acer saccharum*) in the Allegheny plateau [39], with addition of dolomite in the latter also increasing the Ca and Mg contents of leaves by two and four times, respectively. This result probably reflected a strong improvement in soil conditions, i.e., an increase in exchangeable Ca and Mg, and a decrease in exchangeable Mn and Al. However, there was also a negative effect of a decrease in exchangeable soil K. The decrease in exchangeable soil K was also reflected in the leaves, where K levels decreased by approximately 30% but were presumably not sufficiently low to inhibit growth.

Interestingly, *Prunus serotina* (black cherry) and *Fagus grandifolia* (American beech) did not respond to dolomite application. Clearly, the correct choice of materials for liming of forests depends upon the chemical status of the soils in addition to the pH.

Addition of Mg-containing liming materials or Mg fertilizers to Mg-deficient trees results in a rapid revitalization of the trees as long as the root systems are not irreversibly damaged by soil acidity. Whereas calcite application may have the positive effects of rapidly changing the pH of the soils, increasing exchangeable Ca, and decreasing exchangeable Al, the high levels of Ca may inhibit uptake of both Mg and K. Thus, the calcite application will not decrease Mg deficiency, the main symptom of forest decline, and may lead to induction of K deficiency. Hence, even in terms of base cation supply, the choice of liming materials must be carefully balanced against the site conditions.

4 CONSEQUENCES OF LIMING

4.1 Organic Matter Turnover and N Leaching

Many of the early liming trials carried out in the 1950s to 1960s were stopped when it became apparent that (1) growth was not improved and (2) a too rapid turnover of organic matter may lead to a release of NO₃ to groundwater [46]. In forest soils, the major proportion of soil N storage is in the organic layer. Liming is known to increase the CO₂ evolution from soil organic matter ([27] and references therein) and hence enhance turnover of the humus layer. However, the effect of liming on CO₂ evolution is influenced by a number of factors [27]:

1. Time
2. Soil temperature
3. Soil moisture
4. pH
5. Biological competition and synergism
6. Base-neutralizing capacity of the substrate

In addition, the C/N ratio of the humus material modifies the effect of liming. In soil samples from coniferous forest in Sweden, C/N ratios above 30 ini-
tially enhanced CO₂ evolution [47]. However, after this initial phase, CO₂ evolution was not enhanced but was even negatively affected, which was assumed to be due to N limitation after the easily decomposable matter had been respired. However, if the humus C/N ratio was between 24 and 28, the CO₂ evolution remained continuously enhanced compared with the unlimed treatment. Similarly, in four soil types (brown podzolic soil, humic gley, peaty-gley podzol, peaty-gley ranker), liming caused a net increase in N mineralization that decreased after an initial rapid phase [48]. The greatest decrease was found in the soils with the highest C/N ratios. In the Höglwald experiment [27], higher CO₂ evolution was maintained 2 years after liming, although the C/N ratio was between 28 and 30. This maintenance of higher CO₂ evolution was assumed to be due to atmospheric N deposition that prevented N deficiency. In subsequent years, the site of increased CO₂ evolution moved down the soil profile into the mineral soil as the deacidification front extended downward. The increase in CO₂ evolution was accompanied by a decrease in humus storage on the Höglwald site. The storage of surface humus decreased by 23%, approximately 7.2 t C ha⁻¹, over 6 years. A number of studies have shown that liming leads to a loss of C storage in the humus layer [25,29,36], but there are also a number of exceptions to this [49,50]. Marschner and Wilcynski [36] found a decrease in the C content of the forest floor from 27 to 17% in limed plots, corresponding to a humus loss of 15% in a pine plantation. In oak forests, after 20 months, organic C was reduced from 32 to 23% after liming with calcite [29]. In spruce–fir forest, losses of 80 t C ha⁻¹ from the humus layer were determined, most of which represented redistribution into the mineral soil [36]. In contrast, at the Solling site, both increases and decreases in humus storage [50] or no effect [49] was found.

The decrease in the humus layer after liming has been attributed to increased microbial respiration [25,27]. However, Kreutzer [27] attributed loss of humus layer to other changes such as

1. Leaching of dissolved organic carbon (DOC)
2. Displacement of material rich in C in the mineral soil by the activity of earthworms
3. Redistribution of root mass

Following liming at the Höglwald site, the dissolved organic carbon leaching from the humus layer increased strongly, with a calculated flux of about 2 t C ha⁻¹ over a 7-year period. Similarly, Marschner and Wilcynski [36] found an increase in water-soluble fulvic acids after liming.

The decrease of humus storage at the Höglwald site [27] resulted in 14% lower N storage on the limed plots and a dramatic increase in nitrate concentration in the seepage water under the rooting zone. The increase in NO₃ was not principally due to direct nitrification in the humus layer. Although the efflux of NO₃ was increased, the main component of the N efflux was organic nitrogen. At 40-cm
depth in the mineral soil, the main N efflux was NO₃, suggesting that the organic N was nitrified in the mineral soil. Emission of N₂O, an important greenhouse gas, was not increased by liming [27]. However, the N forms released after liming may be dependent on the liming materials used [25]. Liming of an acid mull humus or a moder humus with calcite or dolomite resulted in increased release of N primarily as NO₃, whereas after addition of gypsum, release of N was primarily as NH₄. The release of NH₄ into deeper soils layers and the production of NO₃ in deeper soil layers are not without consequences for soil acidity. Both can lead to an increase in soils acidity, and NO₃ will also lead to mobilization and transport of Al [2]; as a consequence, acidity is merely transferred to deeper soil horizons.

### 4.2 Retention or Release of Heavy Metals

Heavy metals from atmospheric pollution strongly accumulate in the humus layer of forest soils [51]. Liming at the Grunewald site [25] significantly increased the concentration of Zn, Cu, Cd, and Mn in the organic layer of the forest floor. This was attributed to a decrease in heavy metal solubility at higher pH and fixation of metals from throughfall and litter inputs. However, as a consequence of humus turnover, heavy metals may be released into the lower soil horizons [27]. Heavy metals, such as Cu and Fe, which form stable organic complexes, were shown to increase in the soil solution of a lime plot at Höglwald [27].

### 4.3 Fine Roots and Ectomycorrhizas

Acidification of forest soils leads to large changes in fine root distribution. In a spruce stand, soil acidity increased total fine root biomass but resulted in a much shallower root distribution [18,19] (Fig. 1). With increasing soil acidity, the specific root length (root length per unit dry weight) decreased; i.e., roots became thicker [19]. At the more acid sites of the Harz mountains and the Fichtelgebirge, higher total root biomass was found, but the roots were mainly confined to the organic layer and the 0–10 cm mineral soil layer. In contrast, at the Ebergötzen site, fine roots were found at a depth of 80 cm [19]. The differences in fine root distribution could clearly be related to Ca/Al ratios in the soil [19].

Revitalization of forest stands can be achieved only if the soil conditions are improved sufficiently to promote fine root development. In an investigation of the long-term effects of liming on root development at a number of stands in Sweden, liming with calcite had little effect on fine root biomass [52]. However, the specific root length increased with liming. The stands investigated varied in age (30 to 70 years), and between 5 and 18 years had passed between liming and investigation of the root density. All sites had shown a pH increase in the upper soil layers (see Swedish sites, Tables 1 and 2). A comparison of these results with those of earlier studies on the same sites [52] suggested that the effects of liming may decrease or disappear after 8 to 10 years.
There are a few examples in which liming substantially increased fine root density over the whole soil profile. Huettl and Zoettl [24] reported an increase in root growth in the mineral soil in a Norway spruce stand after addition of water-soluble Mg fertilizers. More significantly, surface liming led to increased shallowness of the root system due to growth proliferation in the limed humus layer (Fig. 2). Hahn [53] showed an increase in the root density in the humus layer 7

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Horizon 0-10 cm</th>
<th>Horizon 10-20 cm</th>
<th>Horizon 20-40 cm</th>
<th>Mean (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebergoetzten</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>0.69 a</td>
</tr>
<tr>
<td>Barbis</td>
<td>a</td>
<td>ab</td>
<td>b</td>
<td>1.38 ab</td>
</tr>
<tr>
<td>Fichtelgebirge</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>1.46 b</td>
</tr>
<tr>
<td>Harz</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>2.08 c</td>
</tr>
</tbody>
</table>

**FIGURE 1** Fine root (<2 mm) biomass and distribution in four Norway spruce (Picea abies) stands growing on soils of differing soil acidity. Shown are the mean values for the soil horizon (0 to 40 or 0 to 20 cm). (Adapted from Ref. 19.)
years after liming. There was no significant change in the total root density of the whole soil profile, and the increase in the root density in the surface humus appeared to be at the expense of the root density in the upper mineral soil; however, this should be interpreted with caution. Such increases in the fine root density in the humus layer after liming are not uncommon. Murach and Schünemann [54] found increased root growth in the humus layer of a Norway spruce stand after liming. Similarly, in a Norway spruce stand limed with dolomite in the Fichtelgebirge, the same effect was found [55]. An increase in the growth of roots in the surface humus was also found in the Swedish sites [53], but there were clear differences between sites, suggesting that liming may not automatically lead to shallower root growth.

**Figure 2** Distribution of fine roots (<1.5 mm) on limed and unlimed plots at the Höglwald site in 1991–1992. The site is an 80-year-old Norway spruce (Picea abies) stand. The limed treatment was limed in 1984 with 4000 kg ha\(^{-1}\) dolomitic lime (Ca/Mg ratio 1.1:1). Shown are the mean values for the soil horizon 0 to 30 cm. (Adapted from Ref. 27, original source Ref. 53.)
The method used to apply lime may prevent surface growth of roots. Application of a liquid dolomite suspension greatly increased root growth in the 10- to 15-cm-deep mineral soil in a young Norway spruce stand [34]. There may also be considerable site and tree species differences in response to surface lime application. However, although there is no firm evidence that increased surface rooting has negative consequences, surface rooting may be undesirable under drought or high windthrow conditions.

Ectomycorrhizas play an important role in the mineral nutrition of trees [56]. Much of the information about the effects of liming on ectomycorrhizas has been gained from studies on sporocarps [57]. However, with the development of molecular identification techniques, it has been shown that aboveground sporocarp-based estimates of fungal diversity correlate poorly with belowground fungal diversity based on root colonization [58]. Based on sporocarp estimations, liming decreased the number of ectomycorrhizal species that produced sporocarps [57,59] and increased the number of saprophytic species producing sporocarps [59]. In investigations using either morphological or molecular identification of ectomycorrhizal fungi on roots, again clear changes in community structure were found [27,58,59]. Although it is well known that the physiological benefits of ectomycorrhizas to trees differ between ectomycorrhiza species [56], the significance of the change in community structure cannot be estimated at present. It is known that ectomycorrhizal community structure is altered by soil acidification [60,61]; however, it is unclear whether the changes induced by liming are a reverse of the acidification affects.

5 FOREST MANAGEMENT

Liming of forest is often carried out after cutting. However, forest harvesting, in particular clear felling, has been shown to decrease humus storage [62] and to increase rates of NO$_3$ runoff [62,63]. The decreased humus storage may be due to an increase in microbial degradation because of increased soil temperatures on clearfelled sites. In an assessment of a number of catchments from clearfelled spruce forests, NO$_3$ was the main strong acid anion produced that led to Al release [63]. In acid beech forests, removal of trees to form forest gaps (30 m in diameter) resulted in a significant decrease in pH at 15 cm soil depth and a significant release of NO$_3$ with the seepage water (80-cm soil depth) [64]. Concentrations of NO$_3$ in the seepage water were between 10 and 18 mg L$^{-1}$ and caused a strong release of Al. The release of NO$_3$ was suggested to be due to decreased root uptake in the gaps, causing a strong disruption of the N cycle. Liming of the gap with 3 t ha$^{-1}$ of fine dolomite strongly reduced the amount of NO$_3$ released with the seepage water. This was suggested to be due to stimulation of growth of herbaceous vegetation after liming, the roots of the vegetation compensating for the lack of NO$_3$ uptake by tree roots. The small size of the gaps prevented significant soil warming. In further work...
[65], in a comparison of the effects of liming on the gaps and the surrounding beech stand, microbial biomass increased in the limed stand but decreased in the limed gap. This was suggested to be due to a decrease in the amount of ectomycorrhizal hyphae in the soil of the limed gap. Emission of N₂O was six times higher at the nonrooted center of the gap than at the rooted edge [66].

As discussed earlier, forest growth may lead to removal of base cations from the soil into tree biomass. Subsequently, tree harvesting may lead to removal of base cations and an increase in the potential for soil acidification. The removal of base cations can be strongly influenced by the harvesting method used [2]. Although the foliage and branches are only 20 to 30% of the biomass of the boles, these parts have much higher nutrient concentrations. As a consequence, there are considerable differences in nutrient removal using whole-tree and bole-only harvesting methods. For Ca, whole-tree harvesting results in two- to three-fold higher removal than bole-only harvesting [13]. Leaving residues on site to mineralize after sawlog harvesting can also greatly replenish Ca in the soil [67]. Fifteen years after harvesting of a deciduous forest in the eastern United States, it was estimated that whole-tree harvesting led to a net loss of Ca of 478 kg ha⁻¹, whereas sawlog harvesting resulted in a net gain of 56 kg Ca ha⁻¹ [2,67]. In beech and spruce forest in Germany, branch removal compared with bole-only removal increased base cation losses by 20% in beech and 100% in spruce [6].

The preceding calculations show that forest-harvesting methods can alter the removal of base cations. However, many of the forest ecosystems in Europe and North America are subjected to high loads of N due to high atmospheric inputs [21,22]. To protect groundwater from excessive NO₃ loads after harvesting, a number of harvesting methods have been suggested [22]. However, these are in part the opposite of recommendations to prevent removal of base cations. For example it has been shown that whole-tree harvesting can greatly limit N losses for the first years after harvesting [22]. Removal of slash not only prevents leaching of N from the slash materials but also promotes rapid regeneration of vegetation cover [68]. Limitation of N losses by liming was also shown in beech forest gaps, which was again attributed to a strong growth and nutrient sink function of the ground flora [66]. In the spruce forest of the Höglwald, although liming stimulated the growth of the ground flora, the nutrient sink function of the shade-tolerant vegetation was insufficient to prevent N losses [69]. This finding suggests that liming to ameliorate soil acidification should best be carried out when the canopy has been opened to improve light conditions. The size of opening in the canopy must be balanced to prevent strong losses of humus storage and hence N due to large changes in micrometeorology. Thus, large-scale clear-cutting and liming before stand reestablishment may not be an appropriate strategy for management of acid forest soils. Rather, soil amelioration should be carried out in small area cuts. Such considerations are particularly important in the restructuring of coniferous plantation forests currently taking place in much of Europe.
6 CONCLUSIONS
It is apparent that the changes brought about by pollution in forest ecosystems can rarely be rectified simply by liming. As is almost always the case, not one single stress factor, in this case acidity, is acting on forest ecosystems. Rather, over a number of years, forests have had to suffer the buildup of a number of stress factors. Hence, a monocausal solution (liming) may have the desired ameliorating effect but may also be the cause of a number of other negative effects. Thus, although liming is the only rapid means of increasing soil pH, it must be considered within the framework of an integrated management system using both chemical amelioration and silvicultural measures.

REFERENCES
54. D Murach, E Schünemann. Die Reaktion der Feinwurzeln von Fichten auf Kalkungs-
55. BV Schnieder, W Zech. The influence of Mg fertilization on growth and mineral con-
tents of fine roots in Picea abies (Karst L.) stands in different stages of decline in NE 
57. R Agerer. Impacts of artificial acid rain and liming on fruitbody production of ecto-
58. T Jonsson, S Kokalj, R Finlay, S Erland. Ectomycorrhizal community structure in a 
59. S Andersson, B Söderström. Effect of lime (CaCO₃) on ectomycorrhizal colonisation 
of Picea abies (L.) Karst. seedlings planted in a spruce forest. Scand J For Res 10: 
60. H Wolf. Identifizierung und Charakterisierung von Ektomykorrhizen auf unter-
schiedlich versauerten Fichtenstandorten. MSc thesis, University of Göttingen, 
Germany, 1998.
with stand age, regional factors, atmospheric pollutants and tree vitality. Agric 
Terrestrial Nitrogen Cycles: Processes, Ecosystem Strategies and Management Imp-
63. C Neal, B Reynolds, J Wilkinson, T Hill, M Neal, S Hill, M Harrow. The impact of 
conifer harvesting on runoff water quality: a regional survey for Wales. Hydrol Earth 
64. J Bauhus, N Bartsch. Mechanisms for carbon and nutrient release and retention in 
beech forest gaps. I. Microclimate, water balance and seepage water chemistry. Plant 
beech forest gaps. II. The role of soil microbial biomass. Plant Soil 168/169: 585–592, 
1995.
66. R Brumme. Mechanisms for carbon and nutrient release and retention in beech forest 
gaps. III. Environmental regulation of soil respiration and nitrous oxide emissions 
67. DW Johnson, DE Todd. Harvesting effects on long-term changes in nutrient pools of 
68. PA Stevens, M Hornung. Effect of harvesting intensity and ground flora establish-
ment on inorganic-N leaching from Sitka spruce plantations in North Wales, UK. 
69. H Rodenkirchen. Nutrient pools and fluxes of the ground vegetation in coniferous 
Role of pH in Phytoremediation of Contaminated Soils

Jianwei W. Huang
Lockheed Martin/REAC, Edison, New Jersey, U.S.A.

Jianjun Chen
University of Florida, Apopka, Florida, U.S.A.

1 INTRODUCTION

Soil contamination by heavy metals, radionuclides, and organic compounds poses significant health risks to humans and animals as well as agricultural production. Contamination of soils has resulted from industrial activities such as mining and smelting, the development of the nuclear industry, the disposal of municipal wastes and sewage enriched with metals, and the use of certain pesticides [1–4]. The remediation of contaminated soils represents a significant expense to many industries and governmental agencies. Soil contamination by toxic metals and radionuclides can be found in almost any country in the world. Because of the large areas of contaminated soils, engineering-based remediation methods, such as excavation, become economically impossible for most of the contaminated sites.

Phytoremediation, the use of plants to remediate contaminated soils, sediments, and waters, has emerged as a cost-effective and environmentally sound alternative for the cleanup of contaminated soils and waters [4–7]. Since the con-
cept of phytoremediation was proposed by Chaney [8], there has been increasing interest in developing phytoremediation technology for the cleanup of contaminated soils [4,9–11]. Phytoremediation of contaminated soils has two major strategies: phytostabilization and phytoextraction. Phytostabilization is the use of plants and soil amendments for physical stabilization of the soil to minimize the migration of contaminants and to induce the formation of insoluble contaminant species that would reduce contaminant bioavailability in the contaminated soil [4,12]. Phytoextraction is the use of plants to remove contaminants from the soils. With the continued cultivation and harvesting of selected plant species at the contaminated sites, the soil becomes decontaminated [5,11,13].

The success of using plants to extract contaminants from soils depends on the bioavailability of the soil contaminants to plant roots and the efficiency of contaminant uptake, translocation, and accumulation by the plants. Soil pH is an important factor affecting adsorption and desorption of contaminants in soils, the availability of contaminants to plant roots, and the transport of contaminants into root cells. This chapter focuses on phytoremediation of soils contaminated by toxic metals and radionuclides and the role of altering soil pH in phytoremediation. For phytoremediation of organic contaminated soils, readers are referred to other publications [14,15].

2 ADSORPTION AND DESORPTION OF CONTAMINANTS IN SOILS

Metal solubility in soils is strongly influenced by soil pH and soil characteristics [16–18]. The main processes associated with the adsorption and desorption of metals in soils are weathering, dissolution and solubility, precipitation, uptake by plants, immobilization by soil organisms, exchange on soil exchange sites, specific adsorption and chemisorption, chelation, and leaching [19]. Most metals are relatively more mobile under acid and oxidizing conditions and are strongly retained under alkaline and reducing conditions [20]. For example, Pb, Zn, Cd, Cu, Co, and Hg are more soluble at pH 4–5 than in a pH range of 5–7 [21]. However, As, Se, and Mo are less soluble under acidic conditions because of the anionic forms of these contaminants.

2.1 Adsorption of Contaminants in Soils

Soil pH can significantly affect the adsorption of heavy metals in soils [17,22,23]. Adsorption of Pb, Cd, Cu, Ni, and Zn by soils was closely correlated with soil solution pH, and increasing solution pH increased metal adsorption [16,24,25]. A linear correlation between Pb and Cd distribution constants and soil pH and organic matter was found for 33 temperate soils [26]. The relationship between metal adsorption and equilibrium soil solution pH was dependent on the initial
metal concentration. At low initial metal concentration, the adsorption of Pb, Cd, Cu, Ni, and Zn was independent of soil solution pH [24]. At high initial concentration, the adsorption of these metals increased when the soil solution pH was increased. The adsorption of As, an anionic contaminant, by soil clay minerals was highest at pH 5 and decreased significantly between pH 7 and 9 [27]. In a comparison of various soil properties (pH, cation exchange capacity, clay content, organic matter, and hydrous Fe and Mn oxide contents), Anderson and Christensen [28] demonstrated that soil pH was the most critical factor affecting the adsorption of Cd, Ni, Zn, and Co in the soils.

2.2 Desorption of Contaminants in Soils

Desorption of Zn, Cu, and Ni from metal-contaminated soils and sludge mixtures increased significantly with decreasing soil pH [29,30]. For each metal, there is a threshold pH value. Above this value, desorption of the metal is little affected by a further increase of soil pH [29,30]. The threshold pH values are 6.3 for Ni, 5.8 for Zn, and 4.5–5.5 for Cu [29,30]. The accumulation of Zn, Cu, and Ni in rye-grass responded to soil pH in a pattern similar to the metal desorption from the soil to the soil solution [29].

In studying the effect of acidification and chelating agents on the solubilization of uranium (U) from contaminated soils, Ebbs et al. [31,32] found that maximum U solubilization was reached in the soil pH range 4–5. The increase of U desorption was coupled with low pH and the presence of chelating agent (citric acid) [32,33]. Citric acid is unique in enhancing soil U desorption because in its free acid form, it is capable of both acidifying the U-contaminated soil and complexing the U in the soil solution. Such reaction would drive U desorption from soil to soil solution [31–33]. In the absence of citric acid, lowering the soil pH by adding elemental S or an inorganic acid such as sulfuric acid or nitric acid had little effect on U desorption from the soil to the soil solution [31–33].

Desorption of As (an anionic contaminant) is increased with increasing soil pH. For example, the soluble arsenic concentration increased 10-fold following liming of As-contaminated soil [34]. Unfortunately, the increased As desorption from soils increases the risk of As contamination of surface water and groundwater in the areas with elevated As levels in the soil.

3 PHYTOSTABILIZATION OF CONTAMINATED SOILS

Phytostabilization is the use of plants and soil amendments to stabilize the soil physically (thus minimizing the migration of contaminants) and to induce the formation of insoluble contaminant species (thus reducing contaminant bioavailability in the contaminated soil) [4,12,35]. Phytostabilization does not remove the contaminants from the soil but inactivates the contaminants in situ. This
form of remediation may be appropriate for certain sites where a short-term risk-reducing practice is acceptable until final remediation of the site can be accomplished [12].

In phytostabilization, soil amendments are applied to contaminated soil; the site is then planted with selected plant species. The plants used in phytostabilization must be effective in contaminant accumulation in roots but less effective in the translocation of the contaminants from roots to shoots [12,35]. The soil amendments for phytostabilization should inactivate contaminants rapidly following application, preventing leaching and minimizing contaminant accumulation in plants. The most promising soil amendments for phytostabilization include alkalinizing agents, phosphates, mineral oxides, organic matter, and biosolids [4,35]. Common alkalinizing amendments are liming agents that have been used to increase soil pH of sludge-amended soils and acid mine spoils to inactivate metal contaminants [12,36]. Liming has to be done periodically to maintain a desired soil pH at which metal contaminants are insoluble.

Phytostabilization has been demonstrated for Pb-contaminated soils [37,38]. After application of P (0.5% of soil weight) or Fe oxyhydroxides (10% of soil weight) to a Pb-contaminated soil, there was a significant shift of the Pb fraction, mostly from the soluble Pb fraction to a nonsoluble fraction [38]. The soil amendments producing such a shift in Pb sequential extraction reduced Pb accumulation in plant shoots by more than 90% [35,39]. Furthermore, Pb bioavailability, estimated by an in vitro simulated mammalian digestive assay [40], was reduced by more than 45% in Pb-contaminated soils after phytostabilization [35]. Growing Agrostis capillaris in Pb- and Zn-contaminated mine wastes, Cotter-Howells and Caporn [41] observed the formation of pyromorphite (Pb-phosphate minerals) from soil Pb and phosphate, demonstrating the role of certain plants in reducing Pb bioavailability. Phosphate amendments (phosphoric acid, phosphate fertilizers, or by-products high in P) are effective in inducing the formation of insoluble forms of Pb [37,42]. Application of P to Pb-contaminated soils produces pyromorphites that are insoluble even under strong acid conditions [43,44].

During the process of phytostabilization, the dense root systems play an important role in stabilizing the soil and preventing erosion by wind and rain [12,45]. Plants also help to minimize water percolation through the soil profile, thus reducing contaminant leaching. Plant roots can also provide surfaces for sorption or precipitation of contaminants [12]. The main advantage of phytostabilization is that it is easy to implement with low operating costs. Phytostabilization can be adapted to a range of site conditions and remediation needs. However, because phytostabilization does not remove contaminants from the soil, continuous monitoring of the site is needed during and after the process. To remove the contaminants from the soil without removal of the soil itself, phytoextraction technology can be used.
4 PHYTOEXTRACTION OF CONTAMINANTS FROM SOILS

4.1 Metal Speciation and Bioavailability to Plants

Depending on the chemical nature of the metals and soil properties, metals in soils occur in various forms (soluble, exchangeable, complexed, organically bound, oxide, and solid particulate). Two examples are As and Pb. Arsenic is present in most contaminated soils either as As$_2$O$_3$ or as arsenic compounds derived from As$_2$O$_3$. Arsenic may also be present in organometallic forms, such as methylarsenic, H$_2$As$_2$O$_4$CH$_3$, and dimethylarsenic acid, (CH$_3$)$_2$As$_2$O$_3$H, which are active ingredients in many pesticides. Two main redox states, As(III) and As(V), have been found in soils. Arsenic (III) is generally considered more mobile and toxic than As (V) [46]. The forms of Pb can be ionic, oxides, hydroxides, and lead–metal oxyanion complexes. Lead forms both mononuclear and polynuclear oxides and the corresponding hydrates and hydroxides. Lead and Pb-hydroxyl complexes are the most stable species under most soil conditions. These forms of Pb are not readily available to plants. Lead also forms stable complexes with both inorganic (e.g., Cl$^-$, CO$_2$$_3$) and organic ligands (e.g., humic and fulvic acid) in soils. Soluble Pb also reacts with carbonates, sulfides, sulfates, and phosphates to form low-solubility compounds, thus reducing availability to plants [47].

Soil pH is one of the most important factors controlling metal solubility in soils; therefore, soil pH can significantly affect metal availability to plants. The pH interacting with soluble organic matter also affects metal solubility. In soil with a high organic matter content and a pH of 6 to 8, Pb may form insoluble organic Pb complexes. If the soil has low organic matter at the same pH, hydrous Pb-oxide complexes or Pb-carbonate or Pb-phosphate precipitates may form; these Pb forms are not easily absorbed by plant roots [46]. At pH 4–6, the organic-Pb complexes become more soluble and hence may become available to plant roots [46].

The change of soil pH in the rhizosphere because of the release of proton and organic acids from plant roots could significantly affect metal bioavailability to plants. The rhizosphere pH change is often caused by an imbalance in uptake by roots of cations and anions, CO$_2$ respiration, excretion of organic acids from roots, and microbial activity [48,49]. A classic example of root-induced rhizosphere pH change is the plant response to Fe deficiency, whereby roots release protons or phytosiderophores to the rhizosphere [49–51].

Using a pea (Pisum sativum) mutant E107, an Fe hyperaccumulator resulting from increased activity of ferric reductase in roots [52], we found that the Fe deficiency–induced increase of ferric reductase activity was strongly regulated by the pH (unpublished results). At pH 6.0 or below, reductase activity was significantly higher than at pH 6.5 or above. Not only did the accumulation of Fe increase, but there were significant increases in accumulation of other metals such...
as Al, Cu, Mn, Pb, and Zn in this mutant even at relatively low levels (0.1–20 μM) of these metals in the solution (unpublished results).

4.2 Uptake of Contaminants by Roots

Several metal contaminants are also essential plant nutrients (Zn, Cu, Ni, and Mn), and others are not known essential elements for plants (Pb, Cd, U, Hg, and \(^{137}\)Cs). Most metals enter root cells primarily through particular transport systems such as carriers or ion channels. The driving force for metal uptake by roots is the electrochemical potential established by the plasma membrane adenosine triphosphatase (ATPase) [53]. Root cells have a plasma membrane potential ranging from \(-100\) to \(-200\) mV [54,55]. This large electrochemical potential gradient across the root cell plasma membrane drives metals into root cells. Furthermore, the activities of these contaminants in the cytoplasm of root cells must be maintained at very low levels because of the pH and other chemical characteristics of cytoplasm. The lower intracellular activity coupled with a large negative membrane potential become a strong driving force for the influx of these contaminants into root cells.

The plasma membrane divalent-cation channels, which pass cations including Co and Ca [56–58], could be the transport pathways for certain metal contaminants into the root cells. There are experimental data suggesting that Zn, Cu, and Ni are transported into root cells via a common transport pathway [59,60]. Using radioactive tracers, researchers have studied voltage-gated cation channels in the plasma membrane of root cells and identified voltage-dependent Ca channels operating in the root cell plasma membrane [61,62]. Using isolated root cell plasma membrane vesicles, Huang and Cunningham [63] found that Pb could significantly inhibit voltage-dependent Ca channels. The inhibition of the Ca channel activity could result from blockage of the channel by Pb or competition between Pb and Ca for the transport pathway. The results are similar to those found in animal systems where Pb is transported into cells via the Ca channel [64]. If ion channels or ion specific transport systems are the pathways for the transport of these contaminated metals, alteration of the ion channels or transport systems through mutation could alter the specificity of contaminant transport and result in a substantially large amount of metals transported into root cells. Using isolated Arabidopsis Pb-accumulating mutants, Chen et al. [65] demonstrated that Pb-accumulating mutants also accumulated high level of Al, Ca, Cu, Fe, Mg, Mn, Ni, and Zn. The results are similar to those for the Mn-accumulating Arabidopsis mutant and pea bronze mutant [66–68].

4.3 Translocation of Contaminants from Roots to Shoots

For practical reasons, the contaminant concentration in plant shoots is the most important parameter for phytoextraction because the harvested portions of plants
at most contaminated sites are limited to the aboveground parts [13,69]. Most metals are rapidly absorbed by roots; translocation of the absorbed metals to shoots, however, is the limiting step for metal accumulation in shoots. Metal contaminants can be divided into two groups on the basis of their chemical properties [70]. Group 1 includes Ag, Cr, Hg, and Pb, which can be absorbed into roots but not easily translocated from roots to shoots. Group 2 includes Cd, Co, Cu, Mn, Mo, Se, and Zn, which are readily absorbed by roots and translocated to shoots. Plants, however, have mechanisms that limit metal translocation even for metals in group 2 because the photosynthetic apparatus of leaves is sensitive to excessive levels of metals.

In response to excess Cd, Zn, Cu, and Pb, plants produce phytochelatins to complex these metals, thus reducing their phytotoxicity [71]. Using two Arabidopsis mutants—cad1-3, defective in PC synthase, and cad2-1, deficient in γ-glutamylcysteine synthetase activity, Chen et al. [72] studied the response of these mutants to Pb exposure. Compared with the wild type, the Pb concentration in shoots of the two mutants was three fold higher, suggesting that in the wild type Pb is retained in roots by phytochelatins to avoid Pb toxicity in shoots.

There are a number of physiological processes involved in contaminant translocation from roots to shoots. These factors are contaminant unloading into root xylem, long-distance transport within the xylem to the shoots, and contaminant reabsorption from the xylem sap by leaf mesophyll cells. The general model for metals unloading into the xylem vessels involves the absorption of metals from soil solution into the root symplasm and then unloading of the absorbed metals from the xylem parenchyma into mature xylem vessels [59]. For most contaminants, the rate of translocation to shoots is much lower than the rate of absorption of these contaminants. For example, using the shoot-to-root concentration ratio to estimate Pb translocation to shoots, Huang and Cunningham [63] found that for any specific time period, the rate of Pb translocation to shoots is less than 30% of the rate of Pb absorption by the roots. Why is contaminant translocation from roots to shoots generally lower? Of the contaminants pertinent to phytoremediation, most are divalent cations. Once the contaminants are transported into the root cells, they are either precipitated in the cell or chelated with organic compounds. For long-distance transport, the contaminants have to be chelated with chelating compounds available inside the root cells. There are experimental data demonstrating that when synthetic chelates were added to nutrient solution, Pb translocation from roots to shoots increased rapidly [73]. The solution pH was critical in chelate-enhanced Pb translocation. When the solution pH decreased from 5.5 to 3.5, chelate-enhanced Pb translocation from roots to shoots increased 20-fold [73]. Metal accumulation in shoots is critical to the success of phytoextraction. In addition to identifying the hyperaccumulating variant and selection of mutants, use of soil amendments such as chelating compounds to solubilize and chelate metals has been shown to enhance translocation of metals to shoots [69,73,74].
4.4 Plant Species Variation in Metal Accumulation

Plant species vary significantly in metal absorption and translocation. A small number of plant species endemic to metalliferous soils can tolerate and/or accumulate high levels of toxic metals. These plants are called hyperaccumulators if they can accumulate more than 1000 mg kg$^{-1}$ of Pb, Co, or Cr or more than 10,000 mg kg$^{-1}$ of Zn, Mn, or Ni in plant shoots when grown in their natural habitat [75–77]. Accumulation of Zn in *Thlaspi* varies between 10,000 and 43,000 mg kg$^{-1}$. The copper concentration in *Haumaniastrum rosulatum* shoots is about 1000 mg kg$^{-1}$, whereas in *H. katangense* tissue it is as high as 8400 mg Cu kg$^{-1}$ [77]. An As hyperaccumulator was identified from fern species [78]. This fern species can accumulate as much as 15,000 mg As kg$^{-1}$ in the above-ground plant tissue. We compared As accumulation by this fern with a number of different fern species that have a similar growth rate and biomass accumulation and found that the arsenic concentration in this hyperaccumulating fern was approximate 200-fold higher than that of other plant species tested (unpublished results).

To date, there are approximately 400 known metal hyperaccumulators in the world [79]. Some of these metal hyperaccumulators have been tested for phytoextraction of metals from contaminated soils and sludges [10,80,81]. Field studies with Zn, Ni, and Cd hyperaccumulators (*T. caerulescens*, *Alyssum murale*, *A. lesbiacum*, *A. tenium*) demonstrated that these plant species accumulated high levels of Zn and Cd in the shoots [10]. The remediation potential, however, may be limited by these metal hyperaccumulators because of the slow growth rate and lower biomass production. Further studies with *T. caerulescens* and *Silene vulgaris* to remediate Zn- and Cd-contaminated soils have demonstrated similar results [80].

In the last 5 years, there has been increased interest in searching for metal-hyperaccumulating plants capable of producing high biomass [15,63,73,82]. Recent data demonstrate that metal hyperaccumulation can be achieved with selected high-biomass agronomic crops in conjunction with the application of soil amendments to the contaminated soils (see discussion later in this chapter).

In addition to the interspecific variation, intraspecific variation also exists. For example, Chen et al. [65] studied Pb transport in 74 *Arabidopsis* ecotypes and detected significant variation among ecotypes in the tolerance and accumulation of Pb. The tolerance index (TI), defined as the ratio of root length for plants grown on the agar medium with Pb (16 mg kg$^{-1}$) to root length on control medium (no added Pb), ranged from 0.17 to 1.2 [65]. The shoot Pb concentration among 74 *Arabidopsis* ecotypes varied from 80 to 800 mg kg$^{-1}$. The results demonstrate significant intraspecific variations in Pb accumulation by these *Arabidopsis* ecotypes. Identifying plant species with high efficiency for targeted metal accumulation will further reduce phytoextraction costs and accelerate soil cleanup processes.
5 METHODS OF ENHANCED METAL PHYTOEXTRACTION

5.1 Soil Amendments Enhance Metal Accumulation

Plants grown on contaminated soils generally do not accumulate very high concentrations of the targeted contaminants in the aboveground plant parts except for metal hyperaccumulators, such as Zn or Ni hyperaccumulators, as discussed earlier. Most current metal hyperaccumulators have limitations in commercial phytoextraction because of the slow growth and low biomass production by these plants. Extensive research has been conducted in various laboratories to induce metal hyperaccumulation in non–metal-hyperaccumulating plants with high biomass production. With the application of various soil amendments to the contaminated soils, it is now possible to achieve the targeted metal concentrations for commercial phytoextraction [33,69,73,80]. The application of soil amendments could adjust soil pH, increase metal desorption from soil to soil solution, supply the chelating agents to buffer metal activity in the soil solution, and increase the metal translocation from roots to shoots.

Two major limitations of phytoextraction of contaminants from soil are the low metal availability in the soil and the inefficient translocation of the contaminants from roots to shoots. Most contaminants are rapidly accumulated in roots if the contaminants are bioavailable in the plant growth media; however, only a small portion of the absorbed contaminants is translocated from roots to shoots [69,81–83]. The success of phytoextraction becomes dependent on the increase and maintenance of contaminants concentrations in the soil solution and the enhanced translocation of contaminants from roots to shoots. Chelates and other chemical compounds have been used to increase the solubility of metals in plant growth media and could significantly increase metal accumulation in plant [18,36,84,85]. Data from a number of laboratories have demonstrated that chelates, organic acids, and certain chemical compounds can be used to trigger metal hyperaccumulation in several agronomic crops with high biomass production [32,33,69,73].

5.2 Phytoextraction of Lead, Uranium, Cesium 137, and Arsenic

For effective phytoextraction of contaminants from soils, each contaminant has to be considered separately because of its unique solution and soil chemistry and its transport characteristics in plants. In the following sections, we discuss the phytoextraction of Pb, U, 137Cs, and As from contaminated soils and review the current progress in soil amendment–induced hyperaccumulation of these contaminants in selected plant species.

5.2.1 Lead

Lead contamination of soils resulted from industrial and mining activities; the use of Pb in paints, gasoline, explosives, and antispark linings; and the disposal of mu-
nicipal sewage sludges enriched in Pb [1–3]. Lead is considered one of the most frequently encountered heavy metals of environmental concern and is the subject of extensive remediation research [15,39,69]. The remediation of Pb-contaminated soils represents a significant expense to many industries and government agencies [4,15]. There are no reliable reports of plants capable of naturally hyperaccumulating Pb in significantly high concentration. Results from hydroponic and sand culture demonstrated that Pb accumulation in plants increased dramatically as soluble Pb levels in the plant growth media increased [63,82]. However, for most Pb-contaminated soils, Pb in soil solution is usually less than 0.1% of total soil Pb [69].

Early studies have indicated that application of chelates to soils increased Pb accumulation in plants [86,87]. These studies have led to the exploration of using soil amendments to enhance Pb desorption from soil to soil solution and Pb accumulation in plants. As an example, application of a synthetic chelate, N-(2-hydroxyethyl) ethylenediamine-triacetic acid (HEDTA) to a Pb-contaminated soil (total soil Pb 2500 mg kg\(^{-1}\)) resulted in a surge of Pb concentrations in shoots of corn and pea (Fig. 1). Shoot Pb concentrations for both species increased from less than 100 mg kg\(^{-1}\) for the control (no HEDTA addition) to more than 10,000 mg kg\(^{-1}\) for the HEDTA treatment (Fig. 1).

The increase of Pb concentration in plants is positively correlated with the
increase in Pb concentration in soil solution [69]. The physiological mechanism involved in chelate-triggered Pb hyperaccumulation in plants is chelate-enhanced Pb translocation. A greenhouse study demonstrated that after applications of EDTA to the root zone of plants grown in Pb-contaminated soil, Pb concentrations in shoot xylem sap increased linearly with increasing EDTA concentrations (Fig. 2). Compared with the control, addition of EDTA (1 g kg\(^{-1}\)) increased Pb translocation more than 100-fold within 24 hours (Fig. 2).

Phytoextraction of Pb from contaminated soils has been demonstrated on several sites in the United States. For example, Blaylock et al. [88] conducted a 2-year phytoremediation trial at a Pb-contaminated site in Trenton, New Jersey, using successive crops of *Brassica juncea* combined with soil amendments. After one crop, the soil Pb level in 72% of the treated area was reduced to the cleanup level (400 mg kg\(^{-1}\)) specific for residential areas [88].
Of the synthetic chelates tested so far, EDTA was the most effective one in increasing Pb desorption from soil to soil solution and Pb accumulation in plant shoots [69,73]. The chelate-triggered increase in Pb concentration of the soil solution is directly associated with the increase in Pb concentration in the xylem stream, Pb translocation from roots to shoots, and Pb accumulation in plants [13,69]. These results suggest that chelates may eliminate two major limiting factors, low Pb bioavailability and poor Pb translocation, in Pb phytoextraction from contaminated soils.

Several possible mechanisms are involved in the chelate-triggered Pb hyperaccumulation in plants [69]. First, the increase in the Pb level in soil solution by chelate is a major factor; therefore, more Pb is available to plant roots. Second, chelates could buffer Pb activity near the root surface and thereby maintain a constant supply of available Pb to root uptake sites [13,69]. Third, the Pb-chelate complex could be directly absorbed by the roots and translocated from roots to shoots [69]. Using 14C- and 210Pb-labeled EDTA and Pb-EDTA, Vassil et al. [74] confirmed that the Pb-EDTA complex was absorbed by roots and translocated to shoots. Current results indicate that phytoextraction may provide a cost-effective strategy for the cleanup of Pb-contaminated soils [13,33,88]. Environmental concerns will require that the chelate addition to the soil be minimized, and methods for preventing leaching of Pb chelates down the soil profile are required for regions where net infiltration occurs [5,69].

5.2.2 Uranium

Soil contamination with U has resulted from the development of the nuclear industry, which involved the mining, milling, and fabrication of various U products [13,32,33,89]. Uranium contamination poses serious risks to the environment and limits the future use of many sites formerly used for U production and processing. Because engineering-based remediation of U-contaminated soil is very expensive, estimated at $2500 m^{-3} [90], phytoremediation techniques have been developed as an alternative for the cleanup of U-contaminated soils [13,32,33]. As with Pb phytoextraction, the success of U phytoextraction depends on soil U availability to plants, U uptake by roots, and U translocation from roots to shoots. To identify ideal soil amendments to increase soil U availability to plants, researchers have investigated the effect of applying synthetic chelates, inorganic acids, and organic acids on U desorption from soil to soil solution. The results of these studies demonstrate that citric acid is the most effective soil amendment to trigger rapid U desorption from soil to soil solution [32,33,89,91]. Citric acid has been shown to form a binuclear complex that increases the transport of U in the soil [92]. The high selectivity of citric acid for U is due to the high affinity of the uranyl cation (UO$_2^{2+}$) for carboxylate groups from citric acid [92–94].

Application of citric acid to the U-contaminated soil (total soil U 280 mg kg$^{-1}$) increased the U concentration in soil solution more than 200-fold [33]. In
pot experiments, the application of citric acid to the contaminated soil transiently reduced the soil pH by 0.5–1.0 unit [32,33]. The application of nitric acid or sulfuric acid at the same concentration as citric acid also reduced the soil pH by a similar magnitude. However, the increase of U in soil solution caused by nitric acid or sulfuric acid was much less than that by the citric acid [33]. The results suggest that the reduction of soil pH contributed only part of the enhanced soil U desorption. The driving force for the enhanced U desorption by citric acid is the chelation between U and citric acid. As with soil U desorption, citric acid is the most effective soil amendment in triggering U hyperaccumulation in plants [32,33]. Among the species tested so far, the citric acid–triggered U hyperaccumulation was most dramatic in B. juncea, B. chinensis, Amaranthus cruentus, and Beta vulgaris [32,33]. Shoot U concentrations in B. juncea and amaranth increased by more than 1000-fold in response to the application of citric acid to the U-contaminated soil containing a total of 750 mg U kg\(^{-1}\) (Fig. 3).

Uranium hyperaccumulation triggered by citric acid was so rapid that a surge of U concentration in plants was observed within 24 hours after citric acid

![Figure 3](image-url)  
**Figure 3**  Uranium accumulation in shoots of selected plant species grown in a U-contaminated soil with total soil U of 750 mg kg\(^{-1}\) in response to the application of citric acid (20 mmol kg\(^{-1}\) of soil). Plants were grown in the U-contaminated soil for 4 weeks before applying citric acid and were harvested 1 week after the citric acid application. The control denotes the plants grown in the U-contaminated soil in the absence of citric acid treatment. Error bars represent ± SE (n = 3). (Adapted from Ref. 33.)
application and the shoot U concentration reached a steady state 3 days after the citric acid treatment [33]. In this form of U phytoextraction, the plants would contain a very low U concentration before the application of soil amendment. After the application of citric acid, U accumulation in plant shoots would increase rapidly, and the plants could be harvested a few days following the citric acid treatment. Uranium phytoextraction has been demonstrated at various U-contaminated sites in the United States [13,33]. This strategy has advantages in reducing the risk that might have been present by having plants with high U levels in the field for long periods of time. Applying this technique will speed up the removal of U from contaminated soils. Because citric acid is biodegradable, rapidly degrading to carbon dioxide and water [95–97], this technology represents an environmentally friendly alternative for the cleanup of U-contaminated soils.

5.2.3 Cesium 137

Radioactive cesium (137Cs) contamination of soils has resulted from nuclear testing, accidental release, and nuclear energy production. Cesium 137 has a half-life of 30.2 years and has very low mobility in soils, even with high rainfall [98]. The presence of 137Cs in soil and water poses significant health risk to humans and animals. There are several laboratories in universities and private companies that have studied the potential of phytoremediation for the cleanup of 137Cs-contaminated soils [13,99,100]. Application of NH₄ and K to the contaminated soil significantly increased 137Cs desorption from soil to soil solution and 137Cs accumulation in plants [99]. Using a similar strategy for the phytoextraction of Pb and U from contaminated soils, Blaylock and Huang [13] tested effects of applying synthetic chelates, organic acid, and ammonium–potassium fertilizers on 137Cs desorption from soil to soil solution. Of the soil amendments tested, ammonium fertilizers (both ammonium sulfate and ammonium nitrate) were very effective in increasing 137Cs desorption from soil to soil solution. For example, after the application of 10 mmol (NH₄)₂SO₄ kg⁻¹ to a 137Cs-contaminated soil with a total soil 137Cs of 370 pCi g⁻¹, the soil solution 137Cs increased from 0.4 to 4.5 pCi g⁻¹ [13]. The application of ammonium fertilizer increased the shoot 137Cs concentration from less than 200 pCi g⁻¹ for the control to more than 1200 pCi g⁻¹ for both corn and winter wheat (Fig. 4).

In a field study, Lasat et al. [99] investigated the potential of three plant species (Amaranthus retroflexus, B. juncea, and Phaseolus acutifolius) to extract 137Cs from contaminated soil and found a 40-fold difference in 137Cs removal by the plant species tested. Amaranthus removed the largest amount of 137Cs because of the highest 137Cs concentration found in shoots and high shoot biomass produced by this species [99]. Phytoextraction of 137Cs from contaminated soils has been demonstrated at the site of the Chernobyl nuclear power plant, where the accident in 1986 caused 137Cs contamination of soil and water [100]. Of the 20 different soil amendments tested, ammonium salts were the most effective in in-
creasing $^{137}\text{Cs}$ desorption from soil to soil solution \cite{100}. Of the various plant species tested, amaranth cultivars had the highest $^{137}\text{Cs}$ accumulation \cite{100}. Compared with that of Pb and U, phytoextraction of $^{137}\text{Cs}$ from contaminated soils is a bigger challenge because the desorption of $^{137}\text{Cs}$ fixed into the clay minerals is very difficult. Further research is needed to identify plant species that hyperaccumulate $^{137}\text{Cs}$ and to identify soil and foliar amendments that enhance $^{137}\text{Cs}$ phytoextraction.

5.2.4 Arsenic

Arsenic is a major contaminant of soils and waters in the United States and other countries. Arsenic is a known carcinogen and mutagen, is detrimental to the immune system, and contributes to skin, bladder, and other cancers \cite{101,102}. Currently, there is no cost-effective method to clean up As-contaminated soils. The development of a cost-effective method of removing As from soil would accelerate the cleanup process for As-contaminated soils and reduce the risk of As contamination of groundwater and drinking water. Before 1968, inorganic forms of As were used extensively in agriculture as insecticides and herbicides. Frequent application of these chemicals at high rates caused significant As accumulation in...
orchard soils [103]. Inorganic forms of As have since been replaced with organic forms because of their reduced phytotoxicity and overall environmental burden. However, excessive additions of any As compounds can cause pollution of nearby ground and surface waters [104]. Arsenic concentrations as high as 500 mg kg$^{-1}$ have been reported in soils having a history of As pesticide or herbicide applications [105,106].

Because arsenate ($\text{AsO}_4^{3-}$) behaves chemically similarly to phosphate ($\text{PO}_4^{3-}$), phosphorus fertilization of orchard soils contaminated by As increased its solubility and mobility [103]. Heavy applications of phosphate to a soil containing high As displaced up to 80% of the total As in the soil, with the water-soluble As leaching down the soil profile [105]. Increased arsenic toxicity to plants occurred following the application of P fertilizer because of As desorption from the adsorption sites by applied P [105,107]. The desorbed As is absorbed by plant roots and translocated to plant shoots and fruits, thus causing arsenic contamination of the food chain. For example, Creger and Peryea [108] reported that applications of monoammonium phosphate increased the As concentration in apple trees and resulted in severe As toxicity symptoms in these trees grown in As-contaminated orchard soils.

In many acid soils, liming is an effective method for raising soil pH and reducing aluminum toxicity. However, for soils with high As levels, increasing the soil pH could result in an increase in As movement in the soil profile because of the pH dependence of the sorption reaction of As on Fe oxide minerals [34].

Development of the As phytoremediation technology would allow in situ treatment of As-contaminated soils. The phytoextraction of As from contaminated soils could significantly reduce the risk of As contamination of the food chain and drinking water. Because complete removal of surface soils for large areas is impractical, phytoextraction technology has significant advantages for agricultural soils contaminated with low levels of As. We have studied the potential of phytoextraction of As from soils and tested the effects of applying alkalinizing agents on As desorption in soil and accumulation in plants. Of the soil amendments tested, NH$_4$OH was effective in enhancing As accumulation in plants (Fig. 5). However, the bioaccumulation factor (ratio of shoot As concentration to soil As concentration) was much lower for As phytoextraction than for Pb and U phytoextraction. Based on the shoot As concentration in Fig. 5, the bioaccumulation factors for $B. \text{juncea}$ and $B. \text{chinensis}$ were less than 3. Significant improvement in this parameter is needed for effective phytoextraction of As from contaminated soils.

A research team from Dr. Lena Ma’s laboratory at the University of Florida identified a fern species ($Pteris \text{vittata}$) that was able to accumulate As in the shoots to concentrations as high as 15,000 mg kg$^{-1}$ [78]. Greenhouse studies have been conducted to investigate As accumulations in this fern along with other plant species. Preliminary data indicated that this fern accumulated, in the aboveground
plant tissue, an As concentration more than 200-fold higher than any other plant species tested using an As-contaminated soil (J.W. Huang, unpublished results). Based on the As concentration in the soil, this fern has an As bioaccumulation factor of greater than 10 in the absence of any soil amendments (J.W. Huang, unpublished result). We are currently conducting research to demonstrate the potential of using this fern to phytoremediate As-contaminated soil and water.

6 RESEARCH NEEDS

Phytoremediation of soils contaminated by toxic metals and radionuclides has demonstrated good potential at various contaminated sites in the United States and other countries. Despite the significant progress that has been made in transferring phytoremediation technology from laboratory and greenhouse to field applications, continuous research and development are needed in a number of areas. Soil pH plays a critical role in altering contaminant availability to plants and contaminant uptake by roots. Research is needed to examine conditions under which the soil pH changes in the rhizosphere can be induced. For example, acidifying fertilizers such as ammonia sulfate can be used to reduce rhizosphere pH, and alkaliz-

**FIGURE 5** Arsenic accumulation in shoots of three plant species grown in the arsenic-contaminated soil (total soil arsenic, 110 mg kg$^{-1}$) in response to the application of NH$_4$OH (1.5 M kg$^{-1}$ soil). Plants were grown in the contaminated soil for 4 weeks before applying the NH$_4$OH and were harvested 1 week after the treatment (J.W. Huang, unpublished results).
ing fertilizers such as calcium nitrate can be used to increase rhizosphere pH. Plant-induced rhizosphere pH change is important because pH can alter the solubility of contaminants at root zones and enhance contaminant absorption by roots. Compared with indiscriminately acidifying or alkalizing bulk soil, the physiological change of rhizosphere soil pH will significantly reduce the risk of contaminants leaching down the soil profile. A better understanding of the mechanisms involved in soil amendment–enhanced contaminant uptake, translocation, and accumulation in the plants is needed. The elucidation of the mechanisms involved in these processes will help in the identification and possibly the synthesis of new soil or foliar amendments to accelerate the phytoremediation process.

Currently, most available metal hyperaccumulators have limitations in commercial phytoremediation because of their slow growth rate and low biomass production. Therefore, a search for hyperaccumulators that grow rapidly and produce large biomass should be continuously pursued. We should use genetics and molecular biological tools to advance phytoremediation technology. Identifying and transferring the genes responsible for metal hyperaccumulation from specific metal hyperaccumulators to plants with high biomass production could have viable commercial applications [109–111]. In addition, molecular biology has provided insights into the processes of metal uptake, translocation, and accumulation in plants. By integrating knowledge and techniques from soil science, agronomy, engineering, plant genetics, and molecular biology, we can develop an advanced phytoremediation technology to accelerate the cleanup of contaminated soils.

REFERENCES

pH and Phytoremediation of Contaminated Soils


64. JL Tomisg, JB Suszkiw. Permeation of Pb\(^{2+}\) through calcium channels: fura \(^{-2}\) mea-


A horizon, 66
abatement strategies, 85, 88, 101, 106
abiotic stress tolerance, 397
acacia species, 75
*Acer saccharum*, 438
acid budget, 177, 178
acid deposition, 15, 16, 83, 95, 96, 99, 103, 106, 433
acid growth theory, 241
acidic emissions, 226
acidification, 15, 16, 41, 42, 47, 70, *See also* soil acidification
cation:anion balance, 64, 70
critical modeling factors, 180
crop residue type, 68
degradation index, 278
hazard factors, 189
legumes vs. non-legumes, 65
minimizing it, 48, 73
nitrate leaching, 171
nitrogen forms, 71
nutrient leaching, 45
permanent, 50, 75
prediction of, 45
rhizosphere. *See rhizosphere acidification*
risk assessment, 190, 193, 194, 201, 202, 204
risk maps, 23
subsoil, 164, 172, 179
topsoil, 164, 166, 168, 175
under wheat, 159
acidification rates, 19, 25, 121, 124, 126, 129, 175–177, 191, 200, 203, 303, 409
down the profile, 142
acid sulfate soils, 9, 12, 190, 193, 272
acid tolerance
drought tolerance, relationship with, 315
acid topsoils, 309
acidification, 15, 16, 41, 42, 47, 70, *See also* soil acidification
cation:anion balance, 64, 70
critical modeling factors, 180
crop residue type, 68
degradation index, 278
hazard factors, 189
legumes vs. non-legumes, 65
minimizing it, 48, 73
nitrate leaching, 171
nitrogen forms, 71
nutrient leaching, 45
permanent, 50, 75
prediction of, 45
rhizosphere. *See rhizosphere acidification*
risk assessment, 190, 193, 194, 201, 202, 204
risk maps, 23
subsoil, 164, 172, 179
topsoil, 164, 166, 168, 175
under wheat, 159
acidification rates, 19, 25, 121, 124, 126, 129, 175–177, 191, 200, 203, 303, 409
down the profile, 142
acid topsoils, 309
Index

[acidification rates]
acidifying fertilizers, 48, 118, 121, 123, 124, 126, 128
acidity
  net mass flow, 155, 156
subsoil, 267
Acidity Decision Support System, 324
acid-sensitive species, 74, 410
acid-tolerant crops, 379, 390
acid-tolerant species, 74, 313, 315, 418
grasses, 98
Acrisols, 4, 9
Acruadox Haplaudand, 12
active acidity, 269
adsorption of contaminants, 450
adsorption of P, 351, 352
aerosols, 84
Africa, 2, 4, 25, 360
agar-indicator technique, 240–245, 248, 250
AgResearch PKSLime Program, 323, 325
Agricultural Production Systems Simulator, 123, 142, See also APSIM
agriculture
  low input, 23
  row crops, 16
agroforestry, 344, 353
Agrostis capillaris, 452
Agrostis palustris, 74
air pollution, 83, 84, 97, 98
Al(OH)₃, 277, 284, 346–348
Al(OH)₅, amorphous, 348
Al:Na ratio, 301
Alabama, 324
aldehydes, 86
Al-F ion pairs, 276
AlF₂⁺, 280
alfalfa, 44, 64, 70, 146, 151, 172, 255, 272, 273, 353, 415
deep water storage, 419
organic anions, 422
tolerance to Al toxicity, 389
Alfisols, 9, 12, 346
aliphatic-OH, 276
alkalinity, 19, 352–354
downward movement, 353
produce, in, 118
release, 154
removal by plants, 413
transfer of, 19
alkalinization, 21, 164
allantoic acid, 67
allantoin, 35, 67
allelopathy, 361, 378
alley farming, 353
Allium cepa, 247
allophane, 12
Al-NO₃, 276
Alnus glutinosa, 66, 68
Al-OH-PO₄ polymers, 276
AlSO₄⁻, 275, 280, 369
identification, 276
aluminum, 282, 286
aluminosilicates, 141, 277
aluminous minerals, 18
aluminum, 9, 19, 98, 99, 202, 212, 274, 277
complexes, 275–280, 284, 285, 346, 347, 350, 352, 410
dissolution, 157
exchangeable, 9, 12, 16, 277, 278
extractable, 76
hydrous oxides, 157
hydroxide, 202
hydroxide, amorphous, 338
ions, 12
measurement, 281, 284
oxides, 4, 9, 39, 47, 372
soil solution, 278, 282
solid phase, 277
solubility, 4
solution chemistry, 274–276
speciation, 284–286
transport in soil, 155
aluminum activity, 346, 347, 350, 352
gypsum, 369
aluminum phytotoxicity, See also aluminum toxicity
aluminum saturation, 322, 324, 338–340, 342, 347, 365, 366, 368, 369
aluminum-sensitive genotypes, 232, 239, 369, 401
aluminum solubility, 346–348
aluminum tolerance
allele diversity, 398
allelic variation, 396
chromosomal location, 396, 397, 399
gene expression, 401
generic classes, 392
genetic control, 393, 394
loci, 397, 398
marker-assisted selection, 398
markers, 397
molecular genetics, 396, 397, 398, 399
multiple genes, 395, 396
mutations, 393, 396, 399
polypeptides, 400
pyramiding genes, 398, 399
RFLP markers, 397, 399
root tip cDNA library, 401
segregating populations, 395
selection for, 392
single dominant gene, 394, 397
two dominant genes, 394–396
aluminum-tolerance gene, 401
aluminum-tolerant genotypes, 239, 350, 389, 394, 395, 400
aluminum toxicity, 2, 21, 30, 158, 159, 190, 232, 239, 274, 276, 278, 279, 285, 303, 315
Al activity vs concentration, 279
amelioration by calcium, 281
amelioration by organic acid anions, 280
amelioration by organic matter, 352
comparison of soil vs solution culture, 279
genotypic differences in sensitivity, 378
moisture stress, 337
nutrient deficiencies, 351
root exudation, 349
seasonality, 301
aluminum-toxic soils, 286
Alyssum lesbiacum, 456
Alyssum murale, 456
Amaranthus cruentus, 461
Amaranthus retroflexus, 462
amendments, 450
contaminated soils, 457, 459, 460
American beech, 438
amino acids, 276
ammonia, 85, 86, 88
abatement strategies, 108
anhydrous, 68
emissions, 88, 87, 96, 101, 102
oxidation, 86
volatilization, 39, 41, 161, 371, 412
ammonia-based fertilizers, 412
ammoniacal nitrogen, 15–17, 19, 21, 25, 32, 35, 38, 41, 48, 65
ammonification, 37, 38, 40, 50, 342–344, 412, 421
ammonium, 35, 84, 87, 139, 252, 353, 411, 440
assimilation, 35, 36, 40, 68
conversion to ammonia, 38
deposition, 84, 91
manganese toxicity, 270
oxidation, 38
phosphate, 416, 418
ammonium nitrate, 19, 65, 416
cesium-137 contamination, 462
ammonium sulfate, 16, 18, 42, 74, 126, 416
cesium-137 contamination, 462
ammonium uptake, 159, 164, 178
acidification, 234
amorphous minerals, 12
Anabaena variabilis, 372
ancient drainage landscape, 353
Andosols, 9, 12, 277, 351
anhydrous ammonia, 68
animal excreta, 41, 87
animal houses, 87
animal welfare, 88
anion exchange resin, 271
annual grass, 49
annual ryegrass, 177
anodic stripping voltammetry, 283
anthropogenic deposition, 100
anthropogenic pollution, 83
antimony microelectrodes, 251–253, 256
apoplast, 93
apple trees, 464
APSIM, 143, 145–147, 149, 150, 152
crop residues, 152
feedbacks in the model, 159
Nwheat module, 160, 164
parameterization, 160, 162, 166
Residue2 surface residue module, 160
simulations, 160–162, 164, 166, 168, 169
SoilN2 soil nitrogen module, 153, 160
SoilpH module, 160
Soilwat2 water balance module, 160, 170
weeds, 162
wheat, 161
APSIM-SoilpH, 143, 151, 153–159, 180
Arabidopsis, 401, 454–456
Arachis hypogea, 251, See also

groundnut
arbuscular mycorrhizal fungi, 378
ARC/INFO, 198, 204
ArcView, 198
Arenosols, 4, 12
arsenate, 464
arsenic
accumulation in plants, 464
adsorption, 451
desorption, 451
hyperaccumulation, 456, 464
phytoextraction, 463, 464
solubility, 450
speciation, 453
arsenic-contaminated soils, 463
ash, 118
ash alkalinity, 63, 64, 72, 75, 76, 119, 152, 160, 161, See excess cations
Asia, 2, 4, 25, 84, 95, 104, 106
asparagine synthetase, 401
aspartate, 35
Atlantic, 102
atmospheric deposition, 18, 84, 90, 210, 439, 440
atmospheric flux method, 92
atmospheric load, 15
atmospheric N deposition, 439
atmospheric pollution, 440
atomic absorption spectrometry, 273, 281
Australia, 12, 117, 310, 311, 323, 416, 420
acidification, 46
coil waste for acid soils, 339
legume-based pastures, 43
Lime-It, 324
liming, 327
pasture systems, 21
rotations, 50
soil pH, 29
Austria, 101, 106
autotrophic bacteria, 38
aviation, 86
2,2′-azinobis(3-ethylbenzothiazoline-6-
sulfonic acid) (ABTS), 274
Azotobacter, 372
β-glucanase, 401
B horizon, 160
bacteria, 39
Baltic Sea, 102
banana, 21, 141
barley, 50, 243, 270, 272, 273, 350, 399
acid soils, 410
Al tolerance, 350, 399
C:N ratio, 343
base cation content, 4, 15, 344, 345
base cations, 4, 12, 16, 18, 19, 31, 36, 42, 50, 212, 344, 351, 352, 363, 376, 387, 444
depletion of, 15
leaching of, 97, 369, 432, 433
leaching of nitrate, 411, 412
base saturation, 96, 99, 103, 301, 365, 437
Bayerischer Wald, 106
bean, 339, 364–366, 370, 372, 374, 376
Al toxicity, 378
P fertilization, 373
beech, 94, 438, 443, 444
Index

beef, 119, 144
Beer-Lambert law, 244
Belgium, 95, 106
bentgrass, 74
benzene, 281
Beta vulgaris, 461
bicarbonate, 31–33, 51, 139, 147, 150, 155, 156, 177, 233, 234, 317, 320, 352, 434
excretion, 72, 150
ion pairs with Mn, 271
biodiversity, 15, 99
biofertilizer, 372
biogeochemistry, 84
biota, 96, 98, 99
biotic stresses, 94
biotite monzogranite, 194
biserrula, 66
Biserrula pelecinus, 66
black cherry, 438
Black Forest stands, 437
bladder cancer, 463
bogs, 96, 211
boric acid, 273
boron, 71
Bowman-Birk proteinase inhibitors, 401
Brassica campestris, 272
Brassica chinensis, 461, 464
Brassica juncea, 459, 461, 462, 464
Brassica napus, 69, 124, 272, See canola
Brazil, 322, 360, 364, 365
liming requirement, 367
N fertilization, 370
P deficiency, 372
break crops, 419
bromocresol green, 243
bromocresol purple, 240, 242, 243
Brønsted-Lowry alkalis, 153
brown podzolic soil, 65, 439
Brownian diffusion, 91
Bt horizon, 9
buckwheat, 65
Al tolerance, 350
buffering capacity, 15, 21, 48
soil, 47
solution, 233, 234, 237
bulk density, 199
bunch removal, 21
burning stubble, 420
Burundi, 339, 340, 347
C:N ratio, 50, 152, 161, 343, 439
corn, 377
Ca:Al ratio, 98, 223–225, 281, 349, 440
Ca$^{2+}$-channels, 210
CaCl$_2$, 278, 300
CaCO$_3$, 48, 434, 437, See lime
cadmium, 100, 283, 44
hyperaccumulators, 456
solubility, 450
Calamagrostis villosa, 211
calcareous soil, 47, 69
calcite, 434, 436, 437, 438, 439, 440
calcium, 9, 15, 18, 19, 32, 41, 69, 71, 75, 107, 270
availability, 151
deficiency, 303, 306, 348, 351374, 433
removal in tree harvesting, 444
terrestrial ecosystem processes, in, 432
uptake, 159, 210
calcium ammonium nitrate, 16, 126
calcium carbonate, 48, See lime
calcium fulvate, 349
calcium nitrate, 19, 38
Cambisols, 4, 12
Cameroon, 340, 347
CaMg(CO$_3$)$_2$, 434, See also dolomite
Canada, 103
cancers, 463
canola, 124, See also Brassica napus
acid soils, 410
Al tolerance, 350
subsoil N, 419
canopy, 92, 93, 98, 444
nutrient leaching from, 213
capillary electrophoresis, 212
carbohydrates, structural, 33
carbon cycle, 16, 21, 121, 128, 140, 175, 176
assimilation, 33, 35
disulfide, 88
carbonate, 317
minerals, 157
carbonic acid, 31, 37
pK, 231, 233
carbonyl sulfide, 88
carboxylate groups, 58, 340, 410, 421
carboxylic acid, 31, 35, 51, 413
carcinogens, 463
cassava, 378
castor bean, 233
catalytic converters, 86, 101
catena, 192, 201
cation:anion uptake ratio, 35, 44, 58, 65, 68–70, 73
cation:anion balance, 58, , 232, 242, 253, 257
measurement, 59, 63
cation exchange, 96, 140, 157
cation exchange capacity (CEC), 9, 153, 157, 169, 201, 277, 298, 340, 365, 278, 308, 309, 342, 410, 437, See also effective cation exchange capacity
effect of liming, 363
humus, of, 433
cation exchange resins, 271, 285
cation exchange sites, 42
cation leaching, 107
cattle, 87, 119
cDNA library, 401
cell growth
electrogenic processes, 240
cell surface negativity, 281
cell wall elongation, 241
Central Europe, 15, 95, 97, 98
ceramic suction cups, 160
cereal, 407
cropping, 123, 325
cyst nematode, 414
grain, 422
CERES-Wheat, 164
cerrado, 360, 369, 370, 372, 373
cesium-137 phytoextraction, 462, 463
chalk, 17
Chamaecytissus palmensis, 76
charge balance, 33, 58, 59
charged colloids, 409
chelation, 450, 455, 457
chemical equilibrium models, 347
chemisorption, 450
Chenopodium album, 376
Chernobyl Nuclear Power Plant, 462
cherry, 438
chickpea, 65, 66, 69, 71, 146
China, 97, 105, 106
chloride, 213, 268, 349
ion pairs with Mn, 271
chloroform, 273
chloropleth map, 193
Chonqing, 105
2-chloro-6 (trichloromethyl) pyridine, 418
Chromazurol S, 282
chrototropic acid, 284
Cicer arietinum, See chickpea
citrate, 253, 349, 351, 410
exudation under Al stress, 350
citric acid, 69, 410, 451, 460–462
clay, 23, 157, 349, 369, 409
pH buffering capacity, 192, 197
minerals, 2
Clean Air Act, U.S., 103, 104
clearfell sites, 443
citric acid, 69
cluster roots, 69
cO2, 31, 36, 86, 97, 233, 237
assimilation, 43
partial pressure in soil, 161
root respiration, 231
soil air spaces, 37
cobalt solubility, 450
cocksfoot, 415
Index

colluvium, 194
colorimetry, 240, 243, 273, 282, 286
compensatory liming, 434
composts, 338–340, 352
conifers, 37, 94
conservation tillage, 379
contaminated soils, 457, 460, 466
convection, 91
Convention on Long-Range
Transboundary Air Pollution, 101, 103
Coolup sandy soils, 47
Copper, 100, 283, 440
solubility, 450
hyperaccumulation, 456
Al tolerance, 350
mycorrhiza, 378
Pb accumulation, 458
proton fluxes, 241
tolerance to Al toxicity, 389
Corsica, 15
cost:price ratio, 418
cotton, 69, 270, 272, 278, 279
Al toxicity, 378
Coulissenhieb, 211
coulombic attraction, 352
cover crop, 50
cowpea, 270
Al toxicity, 378
crestamento, 391
critical loads concept, 102, 103
crop residues, 152, 160, 161
C:N ratio, 161
crop rotations, 377, 378, 408, 410, 419
crop-pasture ley rotations, 420
crop-pasture rotation, 408, 416, 420, 421
crown ether, 285
CuCl2, 278, 346
cupferron, 273
cyanobacteria, 372
cysteine, 36
cysteine proteinase, 401
cystine, 36
cytoplasmic pH, 35, 58
buffering, 31
regulation, 33
stat, 35
cytoskeleton, 401
cytosolic pH, 58
Czech Republic, 91, 95, 106
Dalrymple Shire, 23
DAP, See diammonium phosphate
deamination, 37, 342
Debye-Hückel equation, 156
decarboxylation, 40, 343–345, 350
organic anions, of, 72
deciduous forest, 37, 76, 444
decision support software system
liming, 324
decomposition of organic matter, 343
deep banding, 417
deep drainage, 146, 172, 409
deep yellow sands, 71
deep-rooted perennial pastures, 415
defoliation, 97
deforestation, 359
2-D electrophoresis, 400
denitrification, 38, 140–142
Denmark, 106
depolarization of membrane, 239
deprotonation, 35
Deschampsia flexuosa, 211
desilication, 4
desorption of contaminants, 451
desorption of P, 351
dialysis, 285
diammonium phosphate, 126, 160, 166, 168, 412, 416
dicalcium phosphate, 42
dicarboxylic amino acids, 35
dicotyledons, 71
diethylthiocarbamate Mn complexes, 273
diffusion, 91, 93
coefficient, 236
diffusivity constants, 161
diffusophoresis, 91
Index

digital elevation models, 190
1,8-dihydroxynaphthlene-3,6-disulfonic acid, 284
3-(2,4 dihydroxyphenylazo)-2-hydroxy-5-chlorobenzene sulfonic acid, 284
dimethylarsenic acid, (CH$_3$)$_2$As$_2$O$_3$H, 453
dimethyl disulfide, 88
dimethyl sulfide, 88
diphenylcarbazone, 273
direct drilling, 50, 421
diseases, 361, 378, 416
resistance, 397
dissociation constant ($pK_a$), 50
dolomite, 118, 374, 434–436, 440, 442, 443
liquid suspension, 443
Douglas fir, 66, 250
drainage, 12, 413, 414
drinking water, 100, 434
drought stress, 2
drought tolerance, 315
dry deposition, 84, 86, 91, 92, 215
duplex soils, 196
dust particles, 84
dye indicators, 240, 241, 257
dystric cambisols, 211
earthworms, 19, 209, 320
East Asia, 106
Eastern Europe, 98
ectomycorrhizas, 443
Eddy correlation, 92, 215
EDTA, 459, 460
effective cation exchange capacity
(ECEC), 322, 368, See also cation exchange capacity
electric currents, 240, 241
electrogenic activity of roots, 241
electro-thermal excitation, 273
engineering-based remediation, 449, 460
enolic-OH, 276
Entisols, 4, 12, 15, 360
Eriochrome cyanine R, 282, 283
ester functional groups, 276
eucalypts, 75
Europe, 15, 19, 84–87, 90, 95–97, 99, 100, 101, 104, 106, 444
European Monitoring and Evaluation Programme, 101
European Union
acidification strategy, 102
emissions of sulfur and nitrogen, 102
energy consumption, 101
eutrophication, 87, 96, 99, 434
evaporation, 93, 161
evaporative demand, 161
evapotranspiration, 29, 162, 414, 432
evacuation, 449
excess anion uptake over cation uptake, 352
excess base, 59
excess cation over anion uptake, 178, 179
excess cations, 35, 59, 63, 64, 72, 75, 76,
See also ash alkalinity
spatial distribution, 179
exchangeable acidity, 12, 47, 299, 301
aluminum, 349, 368
cations, 9, 76
excreta, 149
extension services, 21, 379
faba bean, 253
faeces, 119
Fagopyrum esculentum, 69, See also buckwheat
Fagus grandifolia, 438
fallow, 50, 160, 161, 163, 166, 168, 377, 420
FAO Soil Groups, 4, 9
Faraday cage, 255
farming practice, 21
farming systems, 21
fauna, soil, 99
Fe(OH)$_3$, 365
fence-line contrasts, 21
fens, 15
fern, 456, 464
Ferralsols, 4, 9
ferric-reductase, 453
fertigation, 21
fertilizer number, 124
Fichtelgebirge, 98, 106, 210
fimbrin-like gene, 401
Finland, 101, 437
fir, 436
fish, 98, 100
Fitzgerald River National Park, 194
flocculation-causing anions, 275
flowing solution culture, 270
flue gas cleaning, 86, 90
fluoride, 280
complexation with Al, 275, 276
selective electrometry, 285
fluorimetric methods, 284
Fluvisol, 12
foliar spray, 376
food chain, 464
forage, 415, 422
forage legumes, 377
forests, 2, 15, 19, 91–93, 104
acid deposition, 433, 434
acidification processes, 432
base cation leaching, 433
Ca deficiency, 433
decline, 96, 97, 438
ecosystems, 84, 210
ectomycorrhizas, 443
fertilizing, 224
fine roots, 440–443
floor, 98, 99
heavy metals, 440
liming, 434, 436–444
management, 107
management on acid soils, 444
Mg deficiency, 433
nitrogen saturation, 434
soils, 37, 96
fossil fuels, 15
burning, 83, 85, 86, 90
usage, 104
Frankenwald, 106
free radical formation, 88
freshwater systems, 98
fulvic acids, 276, 283, 340, 351, 410, 439
Pb binding, 453
P adsorption, 352
fungal diversity, 443
fungi, 39, 98, 99
γ-glutamylcysteine synthetase, 455
Gaeumannomyces graminis var. tritici, 390, See also take-all disease
gasoline, 457
genetic variability, 388
genotypic differences in nutrient efficiency, 378
Geographic Information System. See GIS
genetropism, 241
Germany, 90, 91, 95, 97, 98, 106, 433, 363, 374, 444
gibbsite, 275, 277, 280, 338, 347
P adsorption, 352
GIS, 23, 192, 193, 198, 201, 204, 205
raster structures, 192, 193
spatial interpolation of soil properties, 193
vector structures, 192
Gleysols, 12
glutamate, 35
Glycine max, 64, See also soybean
Gmelina tree, 353
goethite, 352
Gossypium hirsutum, 69, See also cotton
GPS coordinates, 198
grain legumes, 50, 66, 71
granite, 172, 211
granitoid gneiss, 194
granodiorite, 194
graphite tube atomizers, 281
grass, 18
grass pastures, 66, 415
grass:legume pasture, 73, 378
GrassGro, 144, 145
grassland, 2, 19
grassland soils, 37
grazed pasture systems, 144
GRAZPLAN, 142–144, 149, 150, 179
simulations, 172–175, 177, 178
soil acidity model, 152, 154, 155, 157, 158
GRAZPLAN soil acidity model, 180
green fallow, 377
green manure, 349, 352
greenhouse gas emissions, 359
groundnut, 251, 253
Al toxicity, 378
groundwater, 100, 434, 444
  quality, 103
  sulfate, 107
guanyurea, 418
gypsum, 2, 269, 348, 349, 361, 369, 374, 369, 415, 440
  requirement, 369
H:C ratios, 154
H⁺/NO₃⁻ symport, 239
H⁺-ATPase pumps, 58
H₂CO₃, 4
H₂S, 39
hard-setting soils, 415
hardwood forest, 15
Haumaniastrum rosulatum, 456
hay, 422
heathlands, 96
heavy metals, 433, 440
  adsorption, 450, 451
  bioavailability, 457
  concentration, 99
  deposition, 98
  desorption, 451
  genotypic differences in accumulation, 456
  hyperaccumulation, 456
  phytoextraction, 453
  phytoaccumulation, 452
  speciation, 453
  species differences in accumulation, 456
  translocation to shoots, 455, 457
  uptake by roots, 454
hedgerow intercropping system, 353
HEDTA, 458
Helianthus annuus, 69, See also sunflower
hematoxylin root staining assay, 392, 394
herbicides, 463
high performance liquid chromatography, 284
Histosols, 4, 12, 15
Hordeum vulgare, 71, See also barley
Hubbard Brook Experimental Forest, 95
human health, 83
humic acids, 276, 283, 340, 347, 351
  lead binding, 453
  P adsorption, 352
humic gley, 439
humic substances, 202
humid regions, 12
  tropics, 4, 21
humification, 202
humus, 153, 154, 161, 433, 434
  accumulation of heavy metals, 440
  C:N ratio, 439
  mor and mull types, 436
  pH, 437
  root density, 441, 442
  storage, 439, 443, 444
hydrocarbon free radicals, 86
hydrocarbons, 86
hydrogen ion leaching, 177
hydrogen peroxide, 274
hydrogen sulfide (SO₂), 88
hydrolyzable acidity, 269
hydrolysis, 274
hydroxy-Al interlayers, 277
2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (NANA), 274
8-hydroxyquinoline, 273, 281, 282, 286
hydroxyl ions, 30, 32, 33, 36, 38, 51, 119, 155, 177, 317, 348, 351, 352, 356
extrusion, 58, 59, 72
hyperaccumulation, 456
hyperpolarization of membrane, 239
ICP-AES, 273, 282, 284, 286
image analysis, 244
imbalance between cation and anion uptake, 118
immobile nutrients, 369
immobilization, 142
Index

[immobilization]
nitrogen, of, 161
immune system, 463
imogolite, 12
Inceptisols, 4, 9, 12, 346, 366, 372
Indian mustard
subsoil N, 419
Indonesia, 106
inductively coupled plasma atomic emission spectroscopy, 273, See also ICP-AES
inertial processes, 91
insecticides, 463
insects, 361, 378, 416
integrated nutrient management, 379
inverse distance weighting, 198, 204
ion chromatography, 212, 285
exchange, 93
fluxes, 236, 238, 239, 242
pairs, 271, 275, 276, 280, 284, 285, 369
selective electrometry, 285
ionic strength, 156, 300, 301, 369
ion-selective microelectrodes, 234, 238, 239
liquid membrane, 234, 235, 236
vibrating, 240
Ipomoea batatas, 270
Ireland, 106
iron, 4, 12, 99
activity, 352
deficiency, 69, 232, 242, 364, 376, 453
deficiency of upland rice, 376
ferric, 242
hydrus oxides, 157, 365
oxides, 4, 9, 39, 47, 372
oxyhydroxides, 452
reduction, 242
toxicity, 158
uptake, 242
irrigation, 88, 146, 361
ISFET (Ion Sensitive Field Effect Transistor) pH measurements, 212
isobutyliden diurea, 49
isoelectric pH, 35
Italy, 90
Japan, 87, 105, 106
Jiangsu, 105
junction potential, 268
kandosol, red, 160
kaolin, 192, 202, 203
kaolinite, 9, 281
Kauri trees, 37
ketonic C==O, 276
kieserit, 434, 437
kikuyu, 272
Klebsiella pneumoniae, 372
kriging, 204
LaCl₃, 278
lactation, 152
lakes, 96, 98
lamb, 119
lambsquarters, 376
land clearing, 409
land managers, 23
land tenure, 327, 389
Langmuir isotherm, 212
latent acidity, 269
lateritic profiles, 202
Lathyrus sativus, 74
laughing gas, 85
leachate, 4
leaching, 15, 16, 18, 19, 37, 66, 92, 107, 450
cover crop, 50
cultivation, 50
intensity, 121
metals, 450
nitrate, 32
nutrients, 41
organic acids, 141
protons, 42
sulfate, 32
lead, 283
complexes, 453
inhibition of Ca channels, 454

Copyright © Marcel Dekker, Inc. All rights reserved.
[lead]
phytoextraction, 457, 458, 459, 460
solubility, 450
speciation, 453
accumulation, 455, 456, 458, 460
desorption from soil, 460
translocation to shoots, 455
lead-accumulating mutants, 454
lead-contaminated soil, 452, 458, 459
lead-phosphate minerals, 452
leaf area index, 163, 168
leaf fall, 151
leaf litter, 99
legumes, 29, 32, 35, 44, 414
cultivation, 85
pastures, 414, 415
species, 21
legume-based
agriculture, 70
pastures, 42, 43, 66, 407
Lehstenbach catchment, 210, 211
lespedeza, 272
Lespedeza striata, 272
Leucaena-based pastures, 141
ley system, 172, 407
lichens, 98, 99
ligand-exchange adsorption, 39, 42
lignin, 343
lime, 1, 17, 19, 23, 42, 46, 75
alkalinity, 317
comparison with organic matter, 345, 346
dissolution, 149, 155, 434, 436
downward movement, 348
equivalents, 124
incorporation in soil, 410
neutralizing value, 323
placement, 317
quality, 323
Lime and Nutrient calculator, 124, 126
lime requirement, 43, 47, 51, 118, 277, 299
components of the decision process, 307–309
definition, 301
[lime requirement]
formula, 367
measurement, 301, 302
tropical soils, 367
lime requirement, biological, 302, 315
lime requirement, maintenance, 316
lime requirement, soil, 302
Lime Responsiveness Index, 311
Lime-It, 324
limestone, 303
liming, 2, 15, 16, 40, 43, 48, 107, 224, 310
arable soils, 311
arsenic concentration, 451
C:N ratio of humus material, 438
definition, 298
economics, 323, 325, 326, 422
ectomycorrhizas, 443
effect, 68, 72
forests, 434, 436–444
graslands soils, 311
increased arsenic mobility, 464
land tenure, 327
longevity of effects, 322
low-input agroecosystems, 338
microbial respiration, 439
nitrate leaching, 438
nutrient interactions, 310
off-site effects, 330
optimal pH, 311
organic matter turnover, 438
overliming, 307
placement, 320, 321
plant responses, 313, 323
root development in forests, 440
social issues, 326–330
tillage, 320
topsoil vs subsoil effects, 317, 319, 320
tropical soils, 363, 365
litter compost, 342
livestock, 15, 101, 376
production, 101, 325
waste, 87
loamy sand, 72
Index

London, 84
Long Range Transport of Air Pollutants, 103
long-range transport models, 90
Lower Saxony, 211, 220
low-input agriculture, 1, 354
low-NOx-burner technologies, 104
lucerne, 146, 151, 172, See also alfalfa
lumogallion, 284
lupin-cereal rotations, 50
lupins, 124, 348, 419
Al tolerance, 350
Lupinus albus, 69
Lupinus angustifolius, 59, See also
narrow-leafed lupin
lupin-wheat rotation, 71
lysimeters, 160, 225
manganese
solution chemistry, 271
MAGIC (Model of Acidification of
Groundwater in Catchments), 212, 225
magnesium, 9, 32, 41, 69, 75, 97, 107, 212, 270
availability, 151
deficiency, 97, 351, 374, 433, 438
fertilizers, 438, 441
forests, in, 224
uptake, 159, 210
magnesium:aluminum ratio, 98, 223, 224
malate, 36, 349, 351
exudation under Al stress, 350
Malaysia, 106
malic acid, 33
malnutrition, 359, 379
manganese, 210, 270, 440
availability, 270, 272
deficiency, 307, 411
exchangeable, 16
measurement, 273
oxides, 271
reduction, 242
speciation, 271
toxicity, 21, 30, 159, 270, 272, 286, 303
[manganese]
uptake, 272
manganese-accumulating Arabidopsis mutant, 454
manganese-iron interaction, 272
manure, 40, 338, 339, 349, 352, 376
integration with inorganic fertilizers, 376
maple, 438
marine aerosol, 90
mass balance models, 103
mass flow, 164, 177
matter flux, 226
meat, 152
Medicago sativa, 64, See also alfalfa
Mehlich-1, 372
Melilotus sp., 272
meliot, 272
membrane potential, 238
Mendelian character, 397
mercury, 100
solubility, 450
Merino wethers, 172
mesofauna, 154
meso-tetra[4-(carboxymethylenoxy)-phenyl]porphyrin [TCMOPPH2], 273
metallothioneins, 401
metals
adsorption, 450, 451
bioavailability, 457
desorption, 450, 451, 457
genotypic differences in accumulation, 456
hyperaccumulators, 456, 457, 466
phytoextraction, 457
speciation, 453
species differences in accumulation, 456
solubility, 450
translocation to shoots, 455, 457
methanol, 284
methionine, 36
methyl isobutyl ketone, 283
methyl mercaptan, 88
methylarsenic, H₃AsO₃CH₃, 453
Mg:Al ratio, 98, 223, 224
MgSO₄, 434, 437
microbial activity, 453
biomass, 154, 444
decarboxylation, 343
decomposition, 350
mineralization, 19
respiration, 439
microelectrodes, 250
microflora, 99
microhabitat, 99
micrometeorology, 444
micronutrient deficiency, 375, 376
foliar sprays, 376
microorganisms, 271
micropotentiometry, 234, 241, 244, 257
micro-suction cups, 248
Milia azedarach, 76
mineral horizons, 19
mineral weathering, 96, See weathering
mineralization, 72, 121, 136, 139, 142, 161–164, 169, 342, 408, 439
pre-season, 168
minimum tillage, 421
mining, 449, 457, 460
Mn-Fe interaction, 272
Mn-toxic soils, 286
mobile nutrients, 369
moder humus, 440
moisture stress, 315
molecular genetics, 391, 396
molybdenum availability, 159
deficiency, 303, 305
solubility, 450
Mongolia, 106
monoammonium phosphate, 412, 416, 464
monomeric Al, 279, 284, 285, 286, 338, 347
mor humus, 436
morin, 285, 286
mosses, 98, 99
mucigel, 352
mucilage, 246
mulch, 353
mull humus, 436, 440
mungbean
Al toxicity, 378
municipal wastes, 449
mutagen, 463
mycorrhizal dependency, 378
mycorrhizas, 378, 443
N serve, 418
narrow-leafed lupin, 59, 65, 66, 69, 70, 71, 74, 124
National Atmospheric Deposition Program, 103
National Precipitation Assessment Program, 103
native ecosystems, 21
natural gas, 104
near-isogenic genotypes, 350
needles, 437
Nernst law, 236
net
acid addition, 149
mineralization rates, 160
present value, 323, 325
Netherlands, 95, 101, 106, 324
Netherlands Institute for Public Health and the Environment, 103
New South Wales, 47, 159, 160, 162, 172, 409
New York, 19
New Zealand, 29, 37, 43, 310, 311, 317, 322
acidification, 46
legume-based pastures, 43
liming, 29, 327
liming of dairy pastures, 325
Northland, 37
NH₃ assimilation, 35 See also ammonia
NH₄⁺-based fertilizers, 75, See ammoniacal fertilizers
n-hexanol, 284
nickel hyperaccumulators, 456
Index

oats, 315
  Al tolerance, 350
occult deposition, 91
OH⁻/NO₃⁻ antiport, 239
O-horizon, 19, 347
oilseed crops, 407
N fertilization, 416
Oklahoma, 388
oligothrophic ecosystems, 96
onions, 247
optimal pH, 388
orchard soils, 464
organic anions, 19, 50, 59, 139–141, 149, 150, 154, 176, 242, 253, 421
amelioration of Al toxicity, 280
carbon cycle, 413
extrusion, 69
export, 152
fate of, 152
mass balance, 152
oxidation, 73, 149, 152
P adsorption/desorption, 352
product removal, 152
removal in produce, 177
organic acids, 37, 44, 50
organic carbon, 16, 23, 154, 169
  conversion to organic matter, 153
organic materials
  acid-amelioration value, 345
  proton consumption capacity, 340
organic matter, 12, 36, 120, 121, 141
  accumulation, 40, 44, 48, 51
  acid subsoils, 347
  Al activity, 351
  Al complexes, 347, 348
  decomposition, 36, 161, 350
decreases with successive cultivation, 369
effects on soil pH, 338–342
measurements, 157
mineralization, 39
nutrient storage, 432
pH-dependent groups, 153
proton flow from soil, 342, 343
root exudation of, 349
organic matter, dissolved, 284, 338, 348, 349, 352, 439
organometallic forms, 453
Ornithopus spp, 66
Oryza sativa, 270, See also rice
osmotic stress, 239
overliming, 307, 376, 390, 411
  micronutrient deficiency, 364
  oxalate, 36, 253, 343
  oxalate oxidase, 401
  oxalic acid, 33
oxidation, 12
Oxisols, 4, 9, 25, 339–341, 344, 345, 347, 348, 351, 360, 364, 365, 368, 379
  Ca and Mg nutrition, 374
  extent of the area, 379
  Fe deficiency, 376
  K deficiency, 373
  N deficiency, 369
  P deficiency, 372
  Zn and B nutrition, 376
oxygen, monoatomic, 86
ozone, 86, 99
paddy rice, 372, See rice
paddy soils, 270
pAl-pH relationship, 161
Panicum virgatum, 272
Papaver somniferum, 272
parent materials, 12
parent rocks, 4
pastures, 19, 71, 301, 323, 414, 415
dairy, 324, 325
legume, 58, 64
legume-based, 310
native, 23
species composition, 173
systems, 16
pasture-ley system, 407
PC synthase, 455
pea, 50, 270, 453
Pb accumulation, 458
peanut, 279, See also groundnut
Index

peat, 338, 339
soils, 211, 321
peaty-gley podzol, 439
ranker, 439
pectins, 33
pedogenic processes, 353
pedotransfer function, 23
penepplain remnants, 194
Pennisetum clandestinum, 272
perennial grasses, 74
   pastures, 419
   species, 409
periodate, 274
permanent charged minerals, 320
permanganate, 273
peroxidase, 401
peroxyacetyl nitrate, 86
persulfate, 273
pesticides, 449, 453
pH, 4
   acidification, 411
   buffer rate, 158
   buffer capacity, 121, 129, 155–158, 168, 169, 191, 192, 197, 199, 252, 302, 311, 341, 411
dye indicators, 240–243, 248
method for expressing, 156
microelectrodes, 58, 250, 251
relationship with clay content, 202
subsoil, 169
topsoil, 169
pH-sensitive glass microelectrodes, 253–256
pH-stat, 234, 257
phalaris, 415
phalaris-based pasture, 49, 74
phase farming, 407, 419
Phaseolus acutifolius, 462
pH-dependent charge, 299
1,10-phenanthroline, 283
phenol red, 243
phenolic acid, 413
phenolic groups, 410
phenolic-OH, 276
phenolphthalein-periodate, 274
phenylalanine ammonia lyase, 401
Phillips River, 194
phosphate, 275
   role in Pb-contaminated soils, 452
   fertilizers, 42
   fixation, 179
   sorption, 179
phosphogypsum, 348, 349
phosphoric acid, 42
phosphorus, 2, 9
   adsorption, 351, 352
   availability, 151, 159, 306
deficiency under Al stress, 350, 351
deposition, 372
desorption, 352
efficiency, 378
fertilization, 436
fertilization under arsenic toxicity, 464
fertilization capacity, 360
phosphorus-use efficiency, 398
photolysis, 85
photo-oxidation, 283, 284
pH-sensitive glass microelectrodes, 253–256
pH-stat, 234, 257
phytochelatins, 455
phytoextraction, 450, 454–457
arsenic, 463, 464
cesium-137, 462, 463
depleted, 457–460
uranium, 460–462
phytoremediation, 449, 450, 455, 456, 460, 462, 464–466
   adsorption of contaminants, 450
desorption of contaminants, 450
phytosiderophores, 242
phytostabilization, 450–452
Picea abies, 210, See also spruce
pig production, 87
pine, 15, 437, 439
Pisum sativum, 70, 270
Planosols, 9
plant materials
   decomposition, 64
Index

plasma membrane, 58
plasma membrane ATPase, 454
platinum, 86
platinum microelectrodes, 253
ploughing, 88, 209
plowing, 88, 209
podzolic soils, 47, 172
Podzols, 4, 12
Podzoluvisols, 4, 9
point of zero charge, 9, 277, 351
policy makers, 21
pollen tubes, 240
pollution of water, 359, 376
polygalacturonate, 352
polymerization, 274
polynuclear Al, 280
poly-olefin resin-coated urea, 49
polyolefin-coated fertilizers, 418
polyphenol, 343
polyploidy, 402
poppy, 272
pores
  fast draining, 213, 224, 225
  slow draining, 213
porphyrins, 276
positional cloning, 402
potassium, 2, 9, 32, 41, 59, 69, 107, 212
  availability, 151
  deficiency, 69, 373
  fertilizer use efficiency, 373, 374
  sulfate, 69
  uptake, 159, 210, 238, 437
potatoes, 324
potentiometry, 234, 250
poultry litter, 342
poultry production, 87
precipitation, 213, 215
precision agriculture, 192
predation pressure, 99
pregnancy, 152
pristine ecosystems, 15, 19, 25
procaryotes, 372
product removal, 121
  acidification, 310
[product removal]
  number, 120
  proteoid roots, 69
  proteomics, 400
proton, 4, 12, 15, 18, 19, 23, 25, 29, 30, 38, 42, 44, 50, 87, 97, 136
  ammonia volatilization, 412
  balance, 413
  balance calculations, 143
  budget, 147, 154, 155, 160
  buffering, 96
  consuming processes, 139, 150
  consumption, 158
  deposition, 94
  downward movement in soil, 73
  extrusion, 58, 59, 64, 70, 71, 147, 150, 151, 159, 164, 178, 232, 253, 352
  historical reports, 257
N cycle, 413
  fluxes, 234, 237, 240, 241, 244, 342, 343
  flux measurement, 232, 233, 234, 236, 237, 240
  net balance, 412
  leaching, 177
  producing processes, 139, 150
  production, 168
  spatial distribution, 179
  toxicity, 159, 268, 280
  proton-calcium exchange, 18
Prunus serotina, 438
Pseudotsuga menziesii, 66, 250
pulse crops, 65, 407, 416, 419
pyrocatechol violet, 282, 283, 286
pyromorphite, 452
Queensland, 23, 202, 277, 310
radiata pine, 75
radioactivity, 449
rainfall, 4, 15, 19, 29, 94
  ammonium in, 32
rainfed, 1
RAINS model, 158
rankers, 12
Index

rape, 272, 273
raster algorithms, 194, 199
raw acid sulfate soils, 12
red alder, 66
red clover, 64
red kandosol, 160
red podzolic soil, 76
redox potential, 253
reduced tillage, 408
Regosols, 12
remote sensing, 190
removal of produce, 118, See acidification
renewables, 85
Republic of Korea, 106
reserve acidity, 278
alkalinization, 164
C:N ratio, 377
decomposition, 153, 351
incorporation, 374
removal, 50
resource-poor farmers, 2
respiration, 154, 413, 439
RFLP mapping, 397
rhizoboxes, 247
*Rhizoctonia cerealis*, 390
rhizoplane, 246
rhizosphere, 58, 231, 232, 246, 351
acidification, 43, 64, 69, 352, 353
heavy metal bioavailability, 453
organic acid anion exudation, 351
pH, 64, 65, 69
pH microelectrodes, 250, 251
phosphorus concentration, 69
redox potential, 253
soil ampling, 246, 247, 248
modifications by fertilizers, 465, 466
root-induced changes, 453
rhizotrons, 248, 249
rice, 270, 272, 364, 366, 370, 371, 374
[rice]
cultivation, 85
lowland, 372, 373, 376
N fertilization, 371, 372
P fertilization, 373
positionional cloning, 402
upland, 373, 374, 376, 378
Richards’ equation, 145
*Ricinus communis*, 233
ripe acid sulfate soils, 12
risk, 189, 190
maps, 23
road transport, 86
rock phosphate, 352
root
apices, 240, 251, 349
architecture, 74
density, 441, 442
growth, 16, 159
growth impairment, 16
hairs, 179, 240, 246, 274
hematoxylin staining, 397
length density, 71, 74
mat, 246
pruning, 2
rot pathogens, 390
tip cDNA library, 401
root:shoot ratio, 97
root-soil interface, 253
rotary harrow, 88
rotations, 410
Rothamsted, 15, 17
runoff, 161, 213, 215, 443
Russian Federation, 106
rye, 315
Al tolerance, 399
ryegrass, 44, 65, 451
 tolerance to Al toxicity, 389
sand over clay soils, 409
sandplain deposits, 194
sandplain soils, 409
sandy clay loam, 160
saprolite, 353
Saskatchewan, 16
Saxony, 211
Schwarzwald, 106
Scotland, 19
Scots pine, 437
sea
  spray, 89
transport, 86
seepage water, 443
selenium solubility, 450
self-limiting effect, 40
semivariograms, 220
sensitivity analysis, 158
serradella, 66
sewage sludge, 342, 349, 458
sharp eye-spot disease, 390
sheep, 119, 144
sheep camps, 152, 177
Sichuan Province, 97, 105
silanization, 235, 236
silcretes, 194
*Silene vulgaris*, 456
silicate, 275, 276
  minerals, 4, 9, 12
siliceous material, 12
  substrates, 4
silicic acid, 59
silicon, 59, 270
SILO Patched Point Dataset, 164
silt, 23, 157
silver fir, 436
silver nitrate, 273
Singapore, 106
skin cancer, 463
slurry, 87, 88, 101
smelting, 449
smog, 84, 86
smoke, 100
smokestack, 83, 84
snapbeans
  Al tolerance, 350
snow sampling, 92
socio-economic factors, 379
sodium, 9, 32, 41, 212
  nitrate, 38
soil
  clay content, 9
  buffering capacity, 15, 21, 23
soil acidification, 15, 29, 97, 107, 117, 310, *See also* acidification
carbon cycle, 413
differences between phases in rotation, 413
ectomycorrhizas, 443
effects of, 98
estimation, 124
long-term effects, 410
management in rotations, 414–418
model, 43
minimization of, 419
N cycle, 411
N fertilizer, 416, 417
nitrate leaching, 416
plant selection, 418, 419
processes in forest soils, 432, 433
product removal, 422
quantifying the components of, 118
relevant concepts, 136
removal of base cations, 444
stratification, 413, 421
stubble management, 420–422
tillage, 420–422
time scale, 411
soil acidity, 1, 2
amelioration, 1, 2
amelioration by organic matter, 338–342
anthropogenic sources, 12
extension program, 2
genetic variability, 388
genotypic differences in tolerance, 313, 315
indices, 365, 366
N fertilizer, 418
Index

[soil acidity]
simulations, 179
soil air, 155
alkalization, 32
amendment, 50
amendments for phytostabilization, 452
biodiversity, 414, 420
biomass pool, 161
biota, 19
buffering, 18, 157
degradation, 359
erosion, 361, 377, 378
fauna, 106, 320, 411
fertility, 360, 361
fertility management, 146, 361
heterogeneity, 210, 213, 215, 225, 246
microflora, 37, 390
mineralogy, 157
moisture, 379
Orders, 9
organic carbon, 157
soil organic matter, 118, 153, 154, 179, 271, 421
cation exchange capacity, 153
maintenance of, 376, 377
pH buffering capacity, 192, 197, 202
subsoil, 203
soil pH, 2, 4, 9, 15, 17, 19, 231
adsorption of heavy metals, 451
aluminum toxicity, 280
amelioration of acidity by organic matter, 342
ammonia volatilization, 39
buffering, 140
complexation of uranium, 451
contaminant availability, 465
controlling aluminum toxicity, 338
effect of undecomposed plant materials, 342–344
measurement, 268, 269, 300, 301
metal solubility, 453
optimal values, 299, 300
optimal values for various crops, 366
phytoextraction of uranium, 461
profile, 178, 307, 309, 310
Soil Profile Acidification Model, 142
soil slicing procedure, 247
soil solution, 103, 220, 222, 224–226, 246, 248, 271, 275, 276, 369
Al activity, 346
Al toxicity, 338
Al$^{3+}$ concentration, 409
contaminant concentration, 457
dominant cations, 320
ionic strength, 300, 301
pH, 269, 280, 450
uranium concentration, 461
soilborne pathogens, 390
SoilWat, 142, 145
solar radiation, 90
Solling, 106, 211
sorghum, 146, 270, 279, 415
Sorghum bicolor, 270, See also sorghum
South Africa, 310
South America, 2, 4, 25, 360
South Australia, 409, 411
South Korea, 105
Southern Hemisphere, 89
Southern Ocean, 194
sowing, 420
soybean, 44, 64, 246, 255, 278, 364, 366, 374, 376, 378
C:N ratio, 343
mycorrhiza, 378
tolerance to Al toxicity, 350, 389
SPAM model, 156
spatial heterogeneity, 217, 218, 219, 225, 226
nitrate, 217, 218, 219
pH, 217, 219, 220
sulfate, 217, 219
speciation programs, 284
spectrophotometer, 243
Spessart, 106
Spirillum lipoferum, 372
split-root, 59, 71
spodic horizon (Bh), 12
Spodosols, 4, 12, 340, 341, 346
sporocarps, 443
spray topping, 414
spruce, 94, 97, 210, 211, 224, 250, 436, 437, 440–444
<table>
<thead>
<tr>
<th>Term</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>spruce–fir forest</td>
<td>439</td>
</tr>
<tr>
<td>stable isotopes</td>
<td>90</td>
</tr>
<tr>
<td>stem flow</td>
<td>92, 93, 213</td>
</tr>
<tr>
<td>stock camps</td>
<td>119, 140</td>
</tr>
<tr>
<td>streams</td>
<td>98</td>
</tr>
<tr>
<td>strengite</td>
<td>351</td>
</tr>
<tr>
<td>strontium chloride</td>
<td>273</td>
</tr>
<tr>
<td>stubble</td>
<td>420</td>
</tr>
<tr>
<td>retention</td>
<td>420, 421</td>
</tr>
<tr>
<td>Stylosanthes</td>
<td>23, 146</td>
</tr>
<tr>
<td>sub-Saharan Africa</td>
<td>360, 372</td>
</tr>
<tr>
<td>subsoil</td>
<td>2, 279</td>
</tr>
<tr>
<td>acidification</td>
<td>72–75</td>
</tr>
<tr>
<td>Al</td>
<td>301</td>
</tr>
<tr>
<td>pH</td>
<td>18</td>
</tr>
<tr>
<td>water</td>
<td>2</td>
</tr>
<tr>
<td>weathered</td>
<td>2</td>
</tr>
<tr>
<td>subsoil acidity</td>
<td>1, 2, 4, 25, 57, 75, 303, 320, 410, 418</td>
</tr>
<tr>
<td>amelioration</td>
<td>320, 348, 349</td>
</tr>
<tr>
<td>subsoiling</td>
<td>320</td>
</tr>
<tr>
<td>subterranean clover</td>
<td>47, 49, 66, 69, 71, 74, 169, 172, 174, 272</td>
</tr>
<tr>
<td>acid soils</td>
<td>410</td>
</tr>
<tr>
<td>overliming</td>
<td>411</td>
</tr>
<tr>
<td>tolerance to acidity</td>
<td>419</td>
</tr>
<tr>
<td>suction cups</td>
<td>211, 212, 220, 226</td>
</tr>
<tr>
<td>ceramic</td>
<td>160</td>
</tr>
<tr>
<td>sugar cane</td>
<td>75, 146, 151, 152</td>
</tr>
<tr>
<td>sugar maple</td>
<td>438</td>
</tr>
<tr>
<td>sugar beet</td>
<td>35</td>
</tr>
<tr>
<td>sulfate</td>
<td>19, 107, 213, 220–222, 275, 348</td>
</tr>
<tr>
<td>immobilization</td>
<td>39</td>
</tr>
<tr>
<td>ion pairs with Mn</td>
<td>271</td>
</tr>
<tr>
<td>leaching</td>
<td>41</td>
</tr>
<tr>
<td>precipitation</td>
<td>225</td>
</tr>
<tr>
<td>sorption</td>
<td>19</td>
</tr>
<tr>
<td>sulphydryl groups</td>
<td>36, 39</td>
</tr>
<tr>
<td>sulfidic clays</td>
<td>12</td>
</tr>
<tr>
<td>sulfur</td>
<td>36</td>
</tr>
<tr>
<td>assimilation</td>
<td>36</td>
</tr>
<tr>
<td>burning process</td>
<td>89</td>
</tr>
<tr>
<td>cycling</td>
<td>32</td>
</tr>
<tr>
<td>deficiency</td>
<td>374</td>
</tr>
<tr>
<td>deposition</td>
<td>91</td>
</tr>
<tr>
<td>elemental</td>
<td>39, 42</td>
</tr>
<tr>
<td>emissions</td>
<td>89, 101</td>
</tr>
<tr>
<td>leaching</td>
<td>32</td>
</tr>
<tr>
<td>oxidation</td>
<td>32, 39</td>
</tr>
<tr>
<td>oxidation/reduction</td>
<td>155</td>
</tr>
<tr>
<td>oxide emission</td>
<td>102–105</td>
</tr>
<tr>
<td>oxides</td>
<td>85, 87</td>
</tr>
<tr>
<td>reduced compounds</td>
<td>12</td>
</tr>
<tr>
<td>tax on</td>
<td>90</td>
</tr>
<tr>
<td>transformation</td>
<td>39</td>
</tr>
<tr>
<td>sulfur dioxide</td>
<td>15, 88, 105, 213</td>
</tr>
<tr>
<td>deposition</td>
<td>95</td>
</tr>
<tr>
<td>emissions</td>
<td>96</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>12, 15, 39, 84, 87, 89, 461</td>
</tr>
<tr>
<td>sulphate deposition</td>
<td>106</td>
</tr>
<tr>
<td>dynamics</td>
<td>212</td>
</tr>
<tr>
<td>sulphoneptaleins</td>
<td>243, 244</td>
</tr>
<tr>
<td>Sumatra</td>
<td>340, 353</td>
</tr>
<tr>
<td>sunflower</td>
<td>69, 70, 268, 270</td>
</tr>
<tr>
<td>superphosphate</td>
<td>42, 173, 276</td>
</tr>
<tr>
<td>superphosphate, triple</td>
<td>376</td>
</tr>
<tr>
<td>surface analysis method</td>
<td>91, 93</td>
</tr>
<tr>
<td>surface waters</td>
<td>103</td>
</tr>
<tr>
<td>sustainability</td>
<td>407</td>
</tr>
<tr>
<td>tropical soils</td>
<td>360</td>
</tr>
<tr>
<td>swamps</td>
<td>15</td>
</tr>
<tr>
<td>Sweden</td>
<td>19, 90, 101, 106, 107, 438</td>
</tr>
<tr>
<td>sweet potato</td>
<td>270</td>
</tr>
<tr>
<td>SWIM (Soil Water Infiltration Movement)</td>
<td>142, 145</td>
</tr>
<tr>
<td>switchgrass</td>
<td>272</td>
</tr>
<tr>
<td>Switzerland</td>
<td>101, 106</td>
</tr>
<tr>
<td>tagasaste</td>
<td>76</td>
</tr>
<tr>
<td>take-all disease</td>
<td>390, 414</td>
</tr>
<tr>
<td>taproot</td>
<td>71</td>
</tr>
<tr>
<td>tartrate</td>
<td>351</td>
</tr>
<tr>
<td>TCMOPPH2-Cd(II)-imidazole</td>
<td>273</td>
</tr>
<tr>
<td>TDR</td>
<td>See time domain reflectometry</td>
</tr>
<tr>
<td>temperate regions</td>
<td>12</td>
</tr>
<tr>
<td>temperature stresses</td>
<td>239</td>
</tr>
<tr>
<td>temporal heterogeneity</td>
<td>220, 225</td>
</tr>
<tr>
<td>sulfate</td>
<td>220</td>
</tr>
<tr>
<td>tensiometers</td>
<td>211</td>
</tr>
</tbody>
</table>
Index

terrestrial ecosystems, 103
3,3',5,5'-tetramethylbenzidine, 273
texture, 160, 161
Thailand, 106
thatch, 19
The Netherlands, 90
The Philippines, 106
*Thlaspi caerulescens*, 456
throughfall, 92–94, 107, 211, 213, 215, 220, 440
tillage, 226, 377, 379, 408, 415, 416, 420, 421
time domain reflectometry (TDR), 160
tipping bucket module, 145
titratable acidity, 278
titrimetry, 232, 233
tobacco, 21
tonoplast, 58
topsoil acidification, 73, 74, 121, 142
subsoil alkalization, 142
topsoil acidification, 73, 74, 121, 142
pH, 18, 25, 47
Torrid Zone, 360
trees, 15
triethanolamine, 273
*Trifolium pratense*, 64, *See also* white clover
*Trifolium repens*, 64, 70, 274
*Trifolium subterraneum*, 66, *See also* subterranean clover
*Trifolium tomentosum*, 66
triticale, 272
Triticeae, 399
*Triticum aestivum*, 65, *See also* wheat
*Triticum turgidum* L. *durum*, 393
tropic of Cancer, 360
tropic of Capricorn, 360
tropical
tropical agriculture, 359
soil fertility, 360
soils, 379
savanna, 360
troposphere, 83, 86
turbulent transport, 91
turnip rape, 272
Typic Sulfaquept, 12
U.S. Great Plains, 387, 390, 392
UK, 106, 311, 322, 323
Ultisols, 4, 9, 12, 16, 25, 340, 341, 344–349, 351, 360
extent of the area, 379
N deficiency, 369
P deficiency, 372
Zn and B nutrition, 376
United States, 87, 310
United States Environmental Protection Agency, 103
unleaded petrol, 105
uranium, 451
hyperaccumulation in plants, 461
phytoextraction, 460–462
urea, 16, 42, 47, 86, 160, 166, 169, 371, 376, 412, 416
enzymatic hydrolysis, 37, 142, 159, 342, 371
foliar application, 371
ureides, 67
urine, 119, 149
deposition, 37
macropore flow, 47
patches, 152, 177, 179

*Vaccinium myrtillus*, 211
variable charge, 9, 12, 39, 308, 309
minerals, 320
soils, 299, 348
surfaces, 277, 278
variable negative charge, 298
variograms, 226
variscite, 351
varzea, 360, 370, 372
vegetation, 83
ventilation system, 88
*Vicia faba*, 253
Victoria, 409
videodensitometry, 244
*Vigna unguiculata*, 270, *See also* cowpea
volatilization, 141
volcanic emissions, 15

---

*Note: The provided text appears to be a page from a book or a document, containing a list of keywords and their related topics or references. It seems to be an index or a table of contents for a book, possibly on environmental science or agriculture. The content includes various terms and locations, which are likely discussed in the subsequent pages of the document.*